

REMARKS

At the outset, applicants thank Examiner Ghali and Examiner Venkat for their time and consideration of the present application at the interview with Bruno Quenon, Veronique Thelliez, Didier Boulinguez, Gaëlle Bourout, Andrew Patch and Philip DuBois.

Claims 19-37 are pending in the present application. Claim 19 has been amended to address a formal matter and to recite that step a) is maintained for 2-5 minutes. Support for the changes to claim 19 may be found in the specification at pg. 15, lines 1-5.

Claims 31-37 recite compositions. While claims 31-37 are new claims, the claimed composition has been examined and considered throughout the prosecution of the present application. The previous Examiner indicated in a telephone conversation on November 4, 2005 that the pending method claims were allowable. Applicants canceled the composition claims in the amendment of February 2, 2006 with the expectation of receiving a Notice of Allowance and then filing a divisional application to further pursue the product claims. However, as the Patent Office maintained the obviousness rejection of the method claims, it follows that the composition claims should be entered and fully considered at this time.

Claims 19-24 were rejected under 35 USC 103(a) as allegedly being unpatentable over U.S. 4,454,161. This rejection is respectfully traversed.

As to claims 19-24, the '161 patent neither discloses nor suggests treating a starch or starch derivative with the time, temperature, and pressure conditions recited in step a) of independent claim 19. The conditions recited in step a) of claim 19 provide that the recited starch or starch derivatives are subjected to a relatively high temperature and pressure for a relatively short duration.

The '161 patent directly treats an amylaceous substance with a branching enzyme, or heats the amylaceous substance prior to the enzymatic treatment to effect the gelatinization and branching of the amylaceous substance. (see column 1, line 50 to column 2, line 20).

Conventional gelatinization conditions use milder conditions than those recited in step a) of claim 19. For example, to gelatinize waxy maize starch, the temperature is generally kept below 92° Celsius, the pressure is typically atmospheric, and the temperature is slowly raised to progressively reach the gelatinization temperature of the starch. Thus, the conditions in the '161 patent stand in contrast to those recited in claim 19.

As the '161 patent fails to disclose or suggest the recited time, temperature and pressure conditions recited in

claim 19, it follows that the '161 patent must produce a composition different from that recited in claims 31-37. In particular, there is no disclosure, either express or inherent, of a composition having the recited amount of α -1, 6 glucosidic bonds or the 1, 6 molecular weight distribution as recited in independent claim 31.

In view of the above, it is believed to be apparent that the '161 patent fails to anticipate or render obvious any of claims 19-24 and 31-37.

At the interview, the Examiners also invited applicant to address how the specification defines the scope for "starch derivatives" and avoids issues under 35 USC 112, first and second paragraphs. Applicant notes in response that the term "starch derivatives" is a term having a well-established meaning in the art. As evidence, applicants firstly submit with the present amendment an entire chapter dedicated to starch derivatives from a starch textbook. That material plainly shows that the term has an art-recognized meaning of involving substances derived from starches that nonetheless maintain characteristics of starches. The term is broader than modified starches, but includes such substances.

Additionally, a review of the United States Patent and Trademark Office database shows that fully 352 U.S. patents issued since 1976 utilize the term "starch derivative" in their

claims. In this regard, the Examiners are respectfully reminded that, under MPEP §1701, office personnel are forbidden to express negative opinions as to the validity of issued patents, except in limited circumstances not present here. And while each case must surely stand on its own facts, it is believed to be quite apparent that any new ground of rejection that would implicitly and necessarily call into question the validity of such a large proportion of the USPTO work product, would be altogether unwarranted. Indeed, the term "starch derivatives" has never been objected to previously during the protracted prosecution of this application, and, in light of the evidence discussed above, no basis is seen for a belated objection at this stage, which objection would be inconsistent with the usage of the term in the art and further inconsistent with the USPTO's own longstanding practice. Thus, it is believed to be apparent that the term does not raise any issues under 35 USC 112, first or second paragraphs.

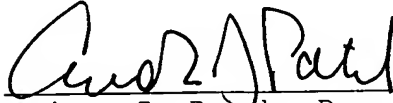
In view of the present amendment and foregoing Remarks, therefore, applicants believe that the present application is in condition for allowance at the time of the next Official Action. Allowance and passage to issue on that basis is respectfully requested.

The Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any

overpayment to Deposit Account No. 25-0120 for any additional
fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17.

Respectfully submitted,

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APPENDIX:

- Rutenberg et al., *Starch Derivatives: Production and Uses*
Starch: Chemistry and Technology, Chapter X, Second Edition,
1984, Academic Press, Inc., ed. Whistler et al.

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STARCH:

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CHAPTER X

STARCH DERIVATIVES: PRODUCTION AND USES

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of the substituent group (acetate, hydroxypropyl); degree of substitution (DS)¹ or molar substitution (MS)¹; physical form (granular, pregelatinized); presence of associated components (proteins, fatty acids, fats, phosphorus compounds) or native substituents.

Starches commonly used for commercial derivatization in the United States are corn, waxy maize, tapioca, and potato. Derivatives of other less available starches such as sorghum, waxy sorghum, wheat, rice, and sago may be offered commercially. The properties, availability in large quantities, and economics are deciding factors in determining which starch is used for derivatization. In Australia, for example, wheat starch is commonly used.

Multiple treatments may be employed to obtain the desired combination of properties. Thus, an acid-converted starch or dextrin may be used for derivatization to obtain a lower viscosity product which is dispersible at higher solids than one made from the native starch and one whose dispersions are still able to be pumped and handled. Hypochlorite-oxidized starch may also be used for further derivatization. Sometimes a derivative made from undegraded starch may subsequently be subjected to the acid-conversion, dextrinization, or oxidation treatment to obtain the desired range of viscosity. Cross-linking is often used in combination with other derivatization treatments to maintain dispersion viscosity upon exposure to high temperature cooking, high shear, or acid. The sequence of the treatments is based on the stability of the substituent groups or the treated starch to subsequent reactions.

The amylose or amylopectin content can be varied by using a high-amylose starch or a starch which is essentially 100% amylopectin (waxy maize starch). Isolated amylose or amylopectin fractions may be used as such.

Most commercially produced derivatives have a DS, generally less than 0.2. Since starch is inherently water-soluble after disruption of the granular structure,

¹The degree of substitution (DS) is a measure of the average number of hydroxyl groups on each D-glucopyranosyl unit which are derivatized by substituent groups. DS is expressed as moles of substituent per D-glucopyranosyl unit (commonly called an anhydroglucose unit and abbreviated as AGU). Since the majority of the AGUs in starch have 3 hydroxyl groups available for substitution, the maximum possible DS is 3. When the substituent group can react further with the reagent to form a polymeric substituent, molar substitution (MS) expresses the level of substitution in terms of moles of monomeric units (in the polymeric substituent) per mole of AGU. Thus, MS can be greater than 3.

$$MS \geq DS$$

$$DS = \frac{162 W}{100 M - (M - 1)W}$$

Where W = % by weight of substituent and M = molecular weight of the substituent, considered as a whole, whether monomeric or polymeric. Where polymeric substituents are present, M and W refer only to the monomeric units of the polymeric substituent and the formula then yields the MS. For example, the DS is used for starch acetates, and MS is used for ethylene oxide-treated starch.

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I. INTRODUCTION

This chapter covers starch derivatives that are produced and marketed in quantities of sufficient size to be considered as commercial scale. However, commercial interest can arise whenever it becomes economically feasible to meet a particular need with a starch derivative which might heretofore have been interesting only from an academic or scientific viewpoint. This commercial interest could result from a unique property, a new, lower-cost method of manufacture, increased demand allowing economies of scale or, perhaps, a completely new and unforeseen application.

The term "starch derivative" includes those modifications which change the chemical structure of some of the D-glucopyranosyl units in the molecule. These modifications usually involve oxidation, esterification, or etherification. Other types of modifications such as hydrolysis (Chapter XVII) and dextrinization (Chapter XX) are the subjects of other chapters, although the products of these modifications may serve as bases for derivatization.

Derivatization of starch is conducted to modify the gelatinization and cooking characteristics of granular starch, to decrease the retrogradation and gelling tendencies of amylose-containing starches, to increase the water-holding capacity of starch dispersions at low temperature thereby minimizing syneresis, to enhance hydrophilic character, to impart hydrophobic properties, and/or to introduce ionic substituents. Modification of starch properties by derivatization is an important factor in the continued and increased use of starch to provide thickening, gelling, binding, adhesive, and film-forming functionality.

A starch derivative is fully defined by a number of factors: plant source (corn, waxy maize, potato); prior treatment (acid-catalyzed hydrolysis or dextrinization); amylose/amylopectin ratio or content; some measure of molecular weight distribution or degree of polymerization (DP, usually described commercially in terms of viscosity or fluidity); type of derivative (ester, ether, oxidized); nature

a relatively high DS is not required to impart solubility or dispersibility as is necessary with cellulose.

1. Manufacture of Derivatives

Low DS derivatives are generally manufactured by reacting starch in an aqueous suspension of 35–45% solids, usually at pH 7–12. Sodium hydroxide and calcium hydroxide are commonly used to produce the alkaline pH. Calcium hydroxide (lime), generally used in suspension because of its limited solubility in water, usually produces some noticeable degradation of starch molecules, presumably because of air oxidation. Sometimes pH is controlled by the metered addition of dilute aqueous alkali, such as a 3% sodium hydroxide solution. Reactions may be done at temperatures ranging up to 60°. Conditions are adjusted to prevent gelatinization of granular starch and to allow recovery of the starch derivative in granular form by filtration or centrifugation and drying. The derivative may be washed to remove unreacted reagent, by-products, salts, and other solubles before final recovery in dry form. To prevent the swelling of starch under strongly alkaline reaction conditions, sodium chloride or sodium sulfate may be added to a concentration of 10–30%. Because the granule gelatinization temperature is lowered as the DS increases, there is a limit to the level of substitution that can be made in aqueous slurry while retaining the starch in granular form.

If the level of hydrophilic substituent becomes high enough, the starch derivative gelatinizes, becomes dispersible at room temperature, and is said to be cold-water-dispersible. These starch granules swell on contact with water due to effects of the introduced hydrophilic groups. Thus, a nonswelling solvent such as isopropanol or acetone, neat or mixed with water, is used to prepare higher DS, cold-water-dispersible derivatives in granule form.

Derivatization is also done by treating the "dry" starch with the required reagents and then heating to temperatures up to 150° to yield granular products of DS up to 1 in granule form. Reagents may be mixed with the starch by dry blending, by spraying an aqueous or nonaqueous solution onto dry starch or a filter cake prior to drying, or by suspending the starch in a solution of the reagents and filtering and drying. Generally, the presence of 5–25% moisture is desirable for efficient reaction. There are some reactions which are more efficient at lower moisture. Derivatives made by this type of semidry reaction often contain salts and reaction by-products as well as unreacted reagent because the product is usually not washed.

Higher DS derivatives containing hydrophobic substituents can be made in water dispersion with recovery of the precipitated product by filtration. Derivatized starches can be recovered from aqueous, dispersed reactions by drum-drying or spray-drying either directly or after removal of salts and low-molecular-weight by-products by dialysis or ultrafiltration.

II. HYPOCHLORITE-OXIDIZED STARCHES

1. Introduction

Although many reagents oxidize starch, alkaline hypochlorite is the most common commercial reagent. Starches oxidized with hypochlorite are termed "chlorinated starches," although no chlorine is introduced into the starch molecules by this treatment. Hypochlorite oxidation has been practiced since the early 1800s. Early work has been extensively reviewed, including investigations with other oxidizing agents such as periodate, dichromate, permanganate, persulfate, chlorite, and hydrogen peroxide (1–3). Oxidants, such as potassium permanganate, hydrogen peroxide, sodium chlorite, hydrogen peroxide, and peracetic acid that have been used to bleach starch are used in such small amounts that the starch is not changed significantly and the products are not considered as oxidized starches. Ammonium persulfate is used in paper mills with continuous thermal cookers to prepare *in situ* high-solids, low-viscosity, aqueous dispersions of degraded starch for coating (4) and sizing operations (5, 6). Hydrogen peroxide is also reported as useful for starch depolymerization in a continuous thermal cooking process (7, 8) as well as on the granular starch (9, 10) or starch derivative (11, 12).

Starch is oxidized to obtain low-viscosity, high-solids dispersions and resistance to viscosity increases or gelling in aqueous dispersion. The oxidation causes depolymerization, which results in a lower viscosity dispersion, and introduces carbonyl and carboxyl groups, which minimize retrogradation of amylose, thus giving viscosity stability.

2. Manufacture

The oxidizing agent is prepared on site by diffusing chlorine into a dilute solution of sodium hydroxide (caustic soda) cooled to about 4°. The concentrations of the caustic and hypochlorite in the reagent solution must be controlled and monitored because excess sodium hydroxide and available chlorine are determining factors in the type of starch modification obtained (643).



Undesirable formation of chlorate is facilitated by temperatures above 30°.

Hypochlorite oxidation of starch is conducted in aqueous slurry with the alkaline sodium hypochlorite solution while controlling the pH, temperature, and concentrations of hypochlorite, alkali, and starch. Since the treatment facilities are usually located at the corn wet-milling plant, starch slurry from the refinery is added to the treatment tank at 18°–24° Bé (approx. 33–44% dry starch). 20,000–100,000 lb (9,000–45,000 kg) of starch may be reacted in a tank equipped with efficient impellers to keep the starch in suspension and to mix the

added reagents rapidly and uniformly. The pH is adjusted to 8–10 with ~3% sodium hydroxide solution, and the hypochlorite solution, containing 5–10% available chlorine, is added during the allotted time. The pH is controlled by addition of dilute sodium hydroxide solution to neutralize the acidic substances produced. The temperature of the exothermic oxidation reaction is controlled to 21°–38° by the rate of addition of the hypochlorite solution or by cooling. A wide variety of products can be made by adjusting the variables of time, temperature, pH, starch, and hypochlorite concentrations and the rate of addition of the hypochlorite.

When oxidation has reached the required level, usually as determined by a viscosity measurement (13, 14), the reaction is stopped by lowering the pH to 5–7 and destroying excess chlorine with sodium bisulfite solution or sulfur dioxide gas. Starch is separated from the reaction mixture by filtration or centrifugation and washed to remove soluble reaction by-products, salts, and carbohydrate degradation products.

3. Oxidative Mechanisms

Investigations of the oxidation of starch by hypochlorite (15–22) and hypochlorite oxidation of amylose (23, 24) and amylopectin (25), as well as the action of chlorine on starch (26–28) and cellulose (29) and the hypobromite oxidation of amylopectin (30) and bromine oxidation of starch (31) have been reported. One investigation indicates that the oxidizing agent penetrates deeply into the granule, apparently acting mainly on the less crystalline areas of the granule. This was indicated by the lack of change in the birefringence (14) and x-ray patterns (15) in oxidized starches. There appears to be a drastic localized attack on some molecules that result in the formation of highly degraded, acidic fragments which become soluble in the alkaline reaction medium and are lost when the oxidized starch is washed (15). Cracks and fissures that develop in oxidized starch have been attributed to this localized overoxidation (15, 32).

The reaction rate of hypochlorite oxidation of amylopectin is markedly influenced by pH (25). The rate is most rapid at pH 7 and very slow at pH 11–13. Similar results were obtained with granular corn starch (20, 21), waxy corn starch, and wheat starch (16). The reaction rate decreases with increasing pH from 7.5 to 10 and remains constant from pH 10 to 11.7 (16). Similar results were noted with amylopectin (25) and amylose (23).

A mechanism for the course of the hypochlorite oxidation was proposed to explain the decrease in reaction rate under acidic and alkaline conditions (20, 21). In acidic medium, hypochlorite is rapidly converted to chlorine which reacts with the hydroxyl groups of starch molecules with the formation of an hypochlorite ester and hydrogen chloride as shown below. The ester then decomposes to a keto group and a molecule of hydrogen chloride. In both steps, hydrogen

atoms are removed as protons from the oxygen and carbon atoms. Thus, in acid medium with excess protons, liberation of protons would be hindered and the rate would be expected to decrease with increasing acidity. Under alkaline conditions, formation of negatively charged starchate ions would occur, increasing with increasing pH. Since negatively charged hypochlorite ion predominates at higher pH, reaction between two negatively charged ions would be difficult because of repulsion. Hence, the oxidation rate would be hindered by increasing pH. Under neutral or slightly acidic or basic conditions, hypochlorite is primarily undissociated and the starch is neutral. Undissociated hypochlorite (hypochlorous acid) would produce starch hypochlorite ester and water, and the ester would decompose to give the oxidized product and hydrogen chloride. Any hypochlorite anion present would act on undissociated starch hydroxyl groups in a similar manner. This hypothesis would explain lower oxidation rates in acidic and basic media and the liberation of acid.

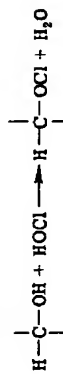
Acid:



Alkaline:



Neutral:



The reaction rate is considerably higher when oxidation is conducted in a starch solution as compared to a suspension of starch granules, indicating that only a part of the granule is available for oxidation (16). At 27° and pH 8.0–10.0, the ratio of reaction rates in gelatinized dispersion and in suspension is constant: for wheat starch, 1.45 at 10.2 g/L; for waxy maize starch, 3.02 at 13.4 g/L and 2.25 at 30 g/L.

Hypochlorite oxidation in an unbuffered starch suspension at pH 10 causes the pH to drop to pH 4. The initial rate at pH 10 is high, drops to a lower rate at pH 8.5, reaches a maximum at about pH 6.2, and then decreases as the pH decreases to about 4. The high initial reaction rate at pH 10 is attributed to soluble starch leaching from the partially swollen granules (about 7.5% of the starch). Correcting for this brings the rate of reaction of the insoluble starch to less than the rate at pH 8.5. About 1–2% of the starch is solubilized at neutral or acid pH (20). The energy of activation for hypochlorite oxidation of wheat starch at pH 8–10 is 21–23 kcal/mole and for waxy maize 16–20 kcal/mole. The reaction rate increases 2–4 times with each 10° rise in temperature (16). The activation energy of corn starch is 17.6 kcal/mole at pH 7.0, 18.4 kcal/mole at pH 8.5, and 23.7 kcal/mole at pH 10.0 (21).

The rate of hypochlorite oxidation of corn starch in a borate buffer is slower than with a carbonate–bicarbonate buffer owing to deactivation of the reactive sites in the starch by complex formation (21).

In oxidation of amylopectin it was found that the conversion of hypochlorite to chlorate is greatest at pH 7 (28.8%). The conversion at pH 3, 5, 9, 10.5, and 12 was 1.5%, 7.1%, 4.6%, 0.7%, and 0.5%, respectively. At pH 3, 5, and 7, the chlorate formed is not an oxidant for amylopectin or hypochlorite-oxidized amylopectin (25). Other workers report no chlorate formation in the pH range 7.5–11.0 at 27° and 37° and less than 2% at 47° (16).

In the hypochlorite oxidation of potato starch, the presence of bromide and cobalt ions exert a catalytic effect at pH 9 and 10, increasing the rate of oxidation as measured by the decrease in active chlorine content, bringing it close to the rate at pH 7. As the active chlorine content of the hypochlorite reaction medium decreases from 30 g/L to 3 g/L, the reaction rate at pH 9–11 becomes more rapid than at pH 7 (19). Nickel sulfate is said to have a catalytic effect on hypochlorite oxidation (33).

4. Chemical Properties

Carboxyl and carbonyl groups are formed by hypochlorite oxidation of starch hydroxyl groups. Scission of some of the glucosidic linkages also occurs, resulting in a decrease in molecular weight. Some of the starch is solubilized and removed during the commercial separation and washing process. Degradative effects induced by the presence of alkali as well as oxidation by atmospheric oxygen can also result in structural changes.

Hypochlorite treatment solubilizes 70–80% of the nitrogen-containing impurities of starch and removes or decolorizes pigmented material (34, 35). Free fatty acid content is reduced by 15–20% on prolonged treatment, with most reduction taking place in the early stages of the reaction.

Whistler and co-workers (23–25, 36) studied the hypochlorite oxidation of

amylose, amylopectin and methyl D-glucopyranosides and found the oxidation to be highly pH dependent. Analysis of potato amylose oxidized at pH 2–12 with 0.1 mole hypochlorite per mole of α -D-glucopyranosyl unit showed an increase in total carboxyl content and a decrease in aldehyde groups with increasing pH while the number of uronic acid carboxyl groups remained about the same. Increasing the concentration of hypochlorite at pH 7 in the oxidation of aqueous suspensions of potato and wheat amylose resulted in increasing numbers of aldehyde and carboxyl groups per AGU¹, with uronic acid carboxyl groups comprising one-half to one-third of the total carboxyl groups (24). Based on data obtained by hydrolysis of hypochlorite-oxidized corn amylopectin and amylose, it was concluded that some of the D-glucopyranosyl units (AGU¹) are not oxidized, even at high levels of oxidant. Further, the isolation of glyoxylic and D-erythronic acids as major products on hydrolysis of hypochlorite-oxidized amylopectin, with a maximum of these products resulting from oxidation at pH 7, suggests initial oxidation at C-2 or C-3 with the formation of a carbonyl group. The formation of an enediol at C-2–C-3 with subsequent oxidation to a dicarboxylated unit in the amylopectin chain was postulated (25). Similar results were obtained in the hypochlorite oxidation of corn amylose in dilute aqueous dispersion at pH 9 and 11, again suggesting initial oxidation at C-2 and/or C-3 to give keto groups which are oxidized further. It was suggested that about 25% of the hypochlorite was consumed in the oxidative cleavage of the C-2–C-3 bonds. The presence of a carbonyl group at C-2 or C-3 leads to depolymerization via β -elimination. A large portion of the hypochlorite is apparently consumed in oxidizing fragments cleaved from the starch chains (23). Alkaline hypochlorite oxidation of methyl 4-O-methyl- α - and β -D-glucopyranosides also indicates preferential oxidation at the C2 and C3 positions, the α form being oxidized at a slower rate (23, 36).

Although the secondary hydroxyl groups are apparently oxidized at a faster rate than are primary hydroxyl groups, the reaction rate on modified starches suggests attack at other sites (20). McKillican and Purves (37) found carboxyl and carbonyl groups in gelatinized wheat starch oxidized by hypochlorite at pH 4.0–4.2. The carboxyl groups appeared to be those of D-glucuronic acid. The carbonyl groups were predominantly aldehyde groups in the C-6 position (65–80%); ~9% were found as keto groups in the C-2 position. Thus, under these conditions, oxidation occurred mainly at the primary hydroxyl group. Hypochlorite oxidation of dispersed wheat starch at about pH 12 gave evidence of attack at the C-2 position followed by cleavage at C-2–C-3, as postulated by Whistler, as well as some oxidation at C-6 (38). Prey and Siklosy (39) found that about 85% of the total carbonyl groups in potato starch oxidized at pH 7–12 with hypochlorite were aldehyde groups, the amount of carbonyl groups decreasing as pH increased.

Hypochlorite oxidation of suspensions of corn starch or high-amylose corn

starch (50% amylose) at pHs above 8.5 for 8 h produced carboxyl and carbonyl groups, in a ratio of very roughly 2:1 (40, 41). An increase in hypochlorite concentration increases the carboxyl and carbonyl group content (39-41). In oxidized potato starch, the ratio of carboxyl to aldehyde groups increases with increasing hypochlorite treatment at pH 8-9, climbing from 0.17 at 5 mg active chlorine per gram of starch to 4.79 at 95 mg/g (42).

Schmorak and co-workers (16-18) investigated the hypochlorite oxidation of granular wheat and waxy corn starches at pH 7.5-11.0. In wheat starch, roughly equal amounts of carboxyl and carbonyl groups were produced at pH 7.5. With increasing pH, the number of carboxyl groups per 100 AGU¹ increased from 1.03 at pH 7.5 to 2.78 at pH 11, while the number of carbonyl groups decreased from 0.91 at pH 7.5 to almost none at pH 9. Waxy corn starch develops 1.5 carbonyl groups per 100 AGU at pH 8, decreasing to 1 per 100 AGU at pH 9 and to practically none at pH 10. The number of carboxyl groups per 100 AGU in hypochlorite-oxidized waxy corn starch increased from 1.0 at pH 8 to 1.4 at pH 9 and 1.8 at pH 10 (16, 17). With an initial hypochlorite concentration of 30 millimoles/liter and a starch concentration of 54 g/L, 5.45% of wheat starch dissolved on oxidation at pH 8, and 1.74% dissolved at pH 10. The apparent DP of the soluble products ranged from 3 at pH 8 to 17 at pH 10 (16, 17).

Schmorak and colleagues (16-18) found that the amylose from wheat starch oxidized with hypochlorite at pH 8 had a number average DP of 131 and a weight average DP of 128 and that glycosidic cleavage was random.

The consumption of about 0.0525 oxygen atoms/AGU during hypochlorite oxidation of wheat starch, as calculated by Schmorak and co-workers (16-18), accompanied by extensive degradation of both amylose and amylopectin components, indicates that scission of each D-glucosidic bond consumes 4-5 oxygen atoms and produces 1-2 carboxyl and 0-1 carbonyl groups. The corresponding figures for waxy corn starch are 2-3 oxygen atoms consumed and about 1.5 functional groups formed per scission.

Hypochlorite oxidation of granular potato starch with cobalt and bromide ion catalysis increases the carboxyl content and shifts the pH maximum for carboxyl group formation from pH 8 without catalyst to about pH 9 (19).

Prey and Fischer (43) investigating hypochlorite-oxidized potato starch found that a stepwise variation of pH from 8 to 10 resulted in a higher proportion of carboxyl groups. A two-step oxidation is claimed to give more rapid oxidation as well as to provide control of the carbonyl:carboxyl ratio (44).

Schmorak and co-workers (16, 17) found that, with wheat starch, the iodine binding capacity does not change much upon oxidation in the pH range 7.5-11.

On the other hand, Fischer and Piller (42) found that, with increasing levels of hypochlorite (5-95 mg Cl₂/g starch) at pH 8-9, there is a decrease in the iodine affinity of the potato starch, reaching a constant low value at about 55 mg Cl₂/g

starch. Based on these results and β -amylase digestibility measurements, they concluded that the amylose is more rapidly degraded than the amylopectin in the initial stages of the oxidation. The lower β -amylase digestibility and iodine binding capacity could also result from the presence of carboxyl and carbonyl substituents in the amylose chain. Degradation of hypochlorite-oxidized starch with amylglucosidase or a mixture of α - and β -amylase shows decreased digestibility with increasing levels of oxidation (45). It was concluded that introduction of a functional group on one AGU¹ protects neighboring units from enzymic attack.

Commercial hypochlorite oxidation of starch under alkaline conditions can also bring about degradative effects. The alkaline degradation of starch has been discussed by BeMiller (46) and Greenwood (47); Corbett (48) has treated the corresponding cellulose reactions.

The presence of carboxyl groups in oxidized starch imparts a negative charge and causes starch granules to absorb methylene blue, a cationic dye. The intensity of the staining is related to the level of electronegativity and hence roughly to the degree of oxidation. Other functional groups such as carboxymethyl, phosphate, or sulfonate will also impart a negative charge and therefore induce staining with methylene blue (49).

5. Physical Properties

Hypochlorite-oxidized starch is supplied in granule form. By virtue of the bleaching effect of the hypochlorite treatment, as well as the solubilization and washing out of protein and associated pigments from, for example, corn starches, the oxidized starch is whiter than is the base starch. Within limits, the degree of whiteness increases with the extent of treatment (50).

In general, oxidized starches are sensitive to heat, tending to yellow or brown when exposed to high temperature. This yellowing tendency during drying has been related to the aldehyde content (51). With increasing aldehyde content, the oxidized starch becomes increasingly yellow on storage (39). Yellowing of oxidized starch dispersed in water by cooking or by alkali is also related to aldehyde content (19).

The hypochlorite-oxidized starch granules exhibit polarization crosses as well as an unchanged x-ray diffraction pattern, indicating that the oxidation takes place mainly in the amorphous regions of the granule (15, 17, 18). Scanning electron microscopy (SEM) shows that the surface of the corn starch granule is unchanged by hypochlorite oxidation up to about 6% active chlorine, with some change apparent at the 8% level (50). Similar results were seen with potato starch (32). Light microscopy shows the presence of fissures developing at the hilum in potato starch granules, extending to the distal poles of the granule and widening

with increased hypochlorite treatment. This indicates that the oxidation takes place in the interior of the granule as well as at the surface. SEM shows hollows in the potato granule after hypochlorite oxidation (32, 52, see also this Volume, Chap. VII).

Although waxy maize starch granules showed no change in size on oxidation, wheat starch granules oxidized at pH 7.5–11.0 with 1 mole of hypochlorite per 20 AGU¹ increased approximately 16% in diameter (16).

The molecular weight distribution of hypochlorite-oxidized wheat starch determined by gel chromatography (22, 53) shows a breakdown of molecules by a second order reaction as oxidation proceeds. Others have found indication of a first-order reaction (16, 20, 21). The intrinsic viscosity of wheat starch, amylose, and amylopectin decreases as the oxidant absorbed increases (17).

Oxidized starches gelatinize at a lower temperature than do native starches when measured by loss of birefringence or by Brabender Viscograph pasting viscosity (13, 49, 54, 55). The shape of the Brabender pasting curve is related to the oxidation conditions. Potato starch oxidized at pH 11 generally has lowest peak viscosity and least paste viscosity stability compared to products made at pH 7–8 (19). Prey and co-workers (54) found that the Brabender peak viscosity decreased and then increased with the amount of hypochlorite treatment of potato starch, although the final viscosity was low for moderate to high oxidant levels (54). Low peak viscosity was observed when granules fragmented without the maximum swelling that occurs with unmodified potato starch. The higher peak viscosity of highly oxidized starch was observed when the granules were greatly swollen although the interiors were solubilized and leached out. The empty hulls collapse rapidly with continued agitation, giving a low final viscosity (15). Changes in viscosity and retrogradation during aging of oxidized potato starch pastes are related to the extent of hypochlorite treatment; higher levels of oxidation produce less retrogradation and viscosity change (56).

Hypochlorite-oxidized starches produce aqueous dispersions of greater clarity and lower viscosity than those of native starch. Further, the dispersions have less tendency to set back or gel. Thus, the pastes are more fluid. Clear solutions are obtained if the degree of oxidation is high (15, 57). The higher the level of hypochlorite treatment, the lower the gelatinization temperature and paste viscosity, the less the setback, and the greater the clarity. Although these effects are found with normal corn starch, it is necessary to use much higher levels of hypochlorite on high-amylose corn starch to obtain increased dispersibility as well as increased clarity and reduced setback (41).

6. Uses

About 80–85% of the hypochlorite-oxidized starch produced is used in the paper industry. It is primarily a paper coating binder where its high fluidity and

good binding and adhesive properties make it effective in high solids pigmented coating colors. Compatibility with the pigment, usually clay, is important and it should not adversely affect water-holding capacity and rheology of the coating color (13, 58–63, 65, 67, 68, see also this Volume, Chap. XVIII).

Until recently, large quantities of oxidized starches were used for paper and paperboard surface sizing to seal pores, tie down loose surface fibers, improve surface strength, and provide holdout of printing inks. Viscosity stability of oxidized starch dispersions as well as the range of viscosities available made them particularly suitable. However, the on-site conversion of native pearl starch by continuous enzyme conversion (69) or thermal-chemical conversion (4, 5, 6, 59) has led to a decrease in the use of oxidized starch in surface sizing and has had some effect on coating use. Thermochemical-converted starch does not have the viscosity stability of the oxidized starch and tends to retrograde on storage making it difficult to use in coating. Methods developed to overcome this retrogradation tendency (70) may lead to a decrease in the use of hypochlorite-oxidized starch in paper coating. Oxidized starch in the wet end of the paper machine, mainly introduced in repulped coated paper (broke), has a detrimental effect on pigment retention by acting as a dispersant (71).

Starch has a long history in the manufacture of textiles; it is used primarily as warp sizing but also in finishing and printing (61, 66, 72, 73). Ground has been lost to synthetic polymers in finishing and to new printing styles. Little starch is used in sizing synthetic filament yarns, and oxidized starches are not used as extensively as other starches in warp sizing. In some instances, the high fluidity, stable viscosity, and flow properties at high solids of oxidized starches allows for greater add-on to the yarn and provides good abrasion protection. Such starches are readily soluble and can be desized from the woven cloth. Oxidized starches may be used in back-filling where a mixture of starch and a filler such as clay is applied to the back of a fabric to fill the interstices of the weave and impart opacity and stiffness. The lower viscosity oxidized starch penetrates fabric to a greater extent than do higher viscosity starches. Finishes are applied to give weight, hand, and draping quality to the fabric. The hypochlorite-oxidized starch may be used, particularly with cotton, in printed fabrics where the less opaque film does not dull colors.

Oxidized starches have been used in laundry finishing, sometimes in aerosol cans for home use. Oxidized starches are also used in the fabrication of construction materials, such as insulation and wall boards and acoustical tile, to provide adhesive, binding, and sizing properties.

Slightly oxidized starches have been used in batters and breadings for foodstuffs such as fried fish where it is claimed to give good adhesion to the food (74–78).

Hypochlorite oxidation provides a convenient method for viscosity reduction in conjunction with other types of modification of starch.

III. CROSS-LINKED STARCH

1. Introduction

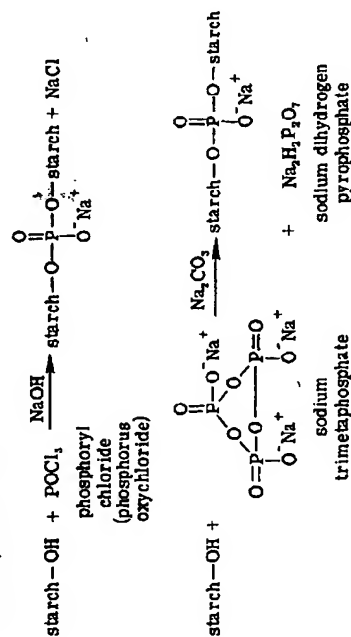
When starch is treated with multifunctional reagents, cross-linking occurs. The reagent introduces intermolecular bridges or cross-links between molecules, thereby markedly increasing the average molecular weight. Because starch contains many hydroxyl groups, some intramolecular reaction which does not increase the molecular weight also takes place. Intramolecular reaction is not significant in the usual granular reactions because the close packing of starch molecules favors intermolecular cross-linking.

Reaction of starch with multifunctional agents may not only be used to interconnect starch molecules but may also be used to bind starch to a substrate such as cellulose (79). Thus, starch-containing wet-rub-resistant paper coatings (65, 80) and water-resistant adhesives (79, 81-83) are produced through formulation with cross-linking agents such as glyoxal and thermosetting resins of the urea-formaldehyde or resorcinol-formaldehyde types. Cross-linking may be effected through weak, temporary bonds such as those formed by the reaction of starch with borax (sodium tetraborate) (644).

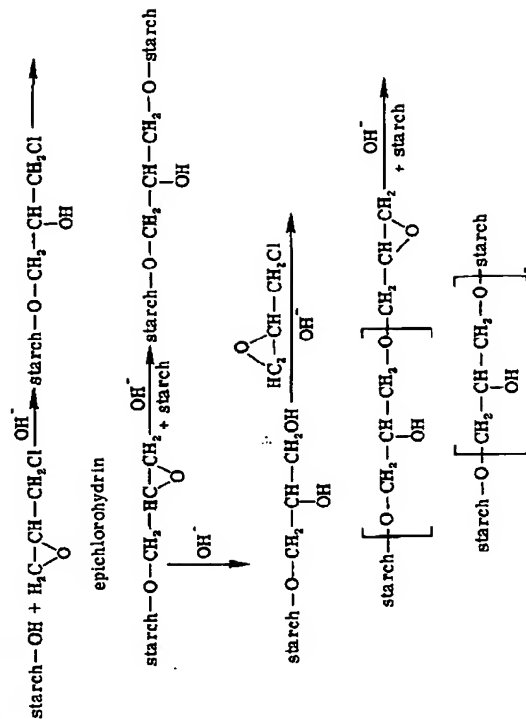
Cross-linking granular starch reinforces hydrogen bonds holding the granule together. This produces considerable change in the gelatinization and swelling properties of the starch granule with reagent in amounts as low as 0.005% to 0.1% by weight of starch. This toughening of the granule leads to restriction in the swelling of the granule during gelatinization, the degree of which is related to the amount of cross-linking. Hence, cross-linking reagents are sometimes referred to as "inhibiting reagents."

2. Preparation

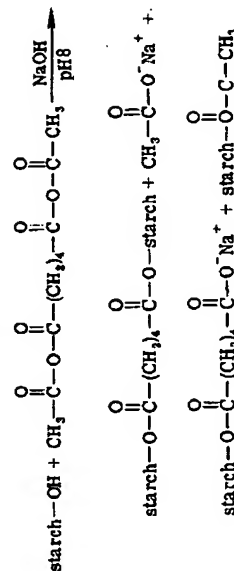
Cross-linking reagent is generally added to an aqueous alkaline suspension of starch at 20°-50°. After reaction for the required time, the starch is recovered by filtration, washed, and dried.



A number of multifunctional cross-linking reagents have been suggested. Maxwell (84) proposed treatment of gelatinized starch or starch derivatives with bifunctional etherifying and/or esterifying agents such as epichlorohydrin, β , β '-dichlorodiethyl ether, or dibasic organic acids reacted under conditions such that both carboxyl groups esterify starch hydroxyl groups. Treatment of granular starch in aqueous alkaline suspension at pH 8-12 with 0.005-0.25% phosphorus oxychloride (phosphoryl chloride) yields a product with high viscosity, even after long cooking or exposure to acid or shear (85). Granules become very resistant to gelatinization when treated with 1% or more of phosphorus oxychloride.



Other common cross-linking agents are epichlorohydrin (86-90), trimetaphosphate (91-94), and linear mixed anhydrides of acetic and di- or tribasic carboxylic acids (88, 95). Still other cross-linking agents include vinyl sulfone (96),



diepoxides (97), cyanuric chloride (98), hexahydro-1,3,5-trisacryloyl-s-triazine (99, 100), hexamethylene diisocyanate and toluene 2,4-diisocyanate (101), *N,N*-

methylenebisacrylamide (102), *N,N'*-bis(hydroxymethyl)ethyleneurea (103), phosgene (104), triphosphate (105), mixed carbonic-carboxylic acid anhydrides (106), imidazoles of carbonic and polybasic carboxylic acids (107), imidazolium salts of polybasic carboxylic acids (108), guanidine derivatives of polycarboxylic acids (109), and esters of propynoic acid (110). Aldehydes, such as formaldehyde (111-115), acetaldehyde (114), and acrolein (116), react bi-functionally to cross-link starch (79), forming acetals. The use of 2,5-dimethoxytetrahydrofuran, as a donor of succinaldehyde via acid hydrolysis, for the acid-catalyzed cross-linking of starch pastes (117) to give a water-resistant adhesive might be applied to granule inhibition. Water-soluble, urea-formaldehyde and melamine-formaldehyde resins have also been claimed as starch cross-linking agents (118, 119). Claims have also been made for cross-linking granular starch with dichlorobutene (120) and less reactive dihalides (86).

The presence of small amounts (0.1-10% on starch) of neutral alkali or alkaline earth metal salts, such as sodium chloride or sulfate, during the cross-linking reaction with phosphorus oxychloride appears to impart better control and a more uniform and efficient reaction, perhaps by retarding hydrolysis of the reagent and thereby increasing penetration into the granule (121). It may be that the salts affect the aqueous environment inside the granule, altering the structure of the water and thereby modifying the juxtaposition of the starch molecules as well as the rate of reagent hydrolysis and penetration. Salts prevent leaching of starch molecules from granules (122).

Inhibited granular starch products may also be made by treatment with a combination of glycine or a glycine precursor and a chlorine-containing oxidizing agent (123). These cross-linkages are heat-labile.

Reactions are conducted mainly in starch slurries. Impregnation of starch with metaphosphate salts at pH 5-11.5, drying, and heating at 100°-160° will also produce a cross-linked distarch phosphate (124).

3. Physical Properties (see also Chapter IX)

Because very low degrees of cross-linking reaction are difficult to determine directly, characterization of cross-linked starches as well as manufacturing in-process and quality control are dependent upon measurement of physical properties such as viscosity, swelling power, solubility pattern, and resistance to shear (125-128). For these measurements, the Corn Industries Viscometer, the Brabender Viscometer, or the Brabender Visco-Amylo-Graph are particularly useful (128-130).

The viscosity of pastes, produced by cooking suspensions of starch, is primarily dependent on the size of swollen, hydrated starch granules. Swollen, hydrated granules, particularly those of potato, tapioca, and waxy corn starches are quite fragile and tend to be fragmented by continued heating or agitation.

Cooking at low pH also causes a rapid breakdown from the initially high paste viscosity (Fig. 1). A cross-linking agent provides covalent bonds which are not readily disrupted by cooking and hold the granule together. Thus, cross-linked granules are less fragile and are more resistant to fragmentation by shear, high temperature, and low pH. Cross-linked starches will maintain higher working viscosities and show less viscosity breakdown than do untreated starches (Fig. 1) (131, 132). At low DS values, the peak viscosity of a cross-linked starch will be higher than that of natural starch. As the amount of cross-linking increases, viscosity breakdown becomes less and the high peak viscosity tends to stabilize. With increasing DS, the peak viscosity disappears and the rate of gelatinization and swelling of the granules decreases, resulting in a continuing increase in viscosity with prolonged cooking. This property can be seen with phosphorus oxychloride-treated potato starch (133) and with tapioca starch reacted with epichlorohydrin, sodium trimetaphosphate, or phosphorus oxychloride (134). Epichlorohydrin is most efficient (Fig. 2).

At high cross-linking levels, granules no longer gelatinize in boiling water (134) nor even under autoclave conditions. Thus, highly cross-linked starch has been used as a dusting powder for surgeon's gloves (90, 92, 112, 135). With intermediate cross-linking, starch is absorbed by the body (90), although there have been some reports of postoperative peritonitis, presumably caused by starch (136, 137).

Cross-linking at low levels will minimize or eliminate the rubbery, cohesive, stringy nature of the aqueous dispersions of waxy corn, tapioca, and potato starch and the accompanying clinging mouth-feel texture that is unpalatable in foods (86, 88, 91, 114, 131). It has been suggested that this viscoelasticity of native root or root-type starches is the result of the interaction of highly swollen,

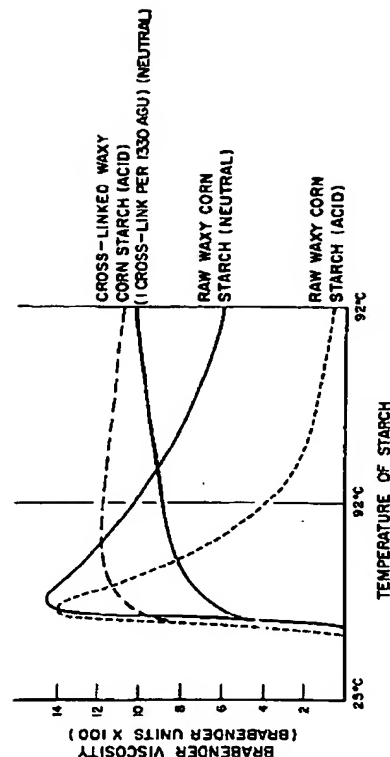


Fig. 1.—Effect of mild cross-linking on viscosity of waxy corn starch and raw waxy corn starch (131).

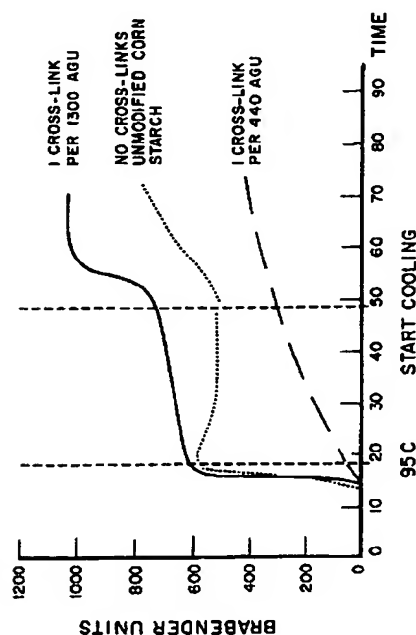


FIG. 2.—Effect of cross-linking on viscosity of corn starch (131).

fragile, hydrated granules so that they interpenetrate, become entangled, and hence generate resistance to flow. Cross-linked granules give little or no interpenetration and, therefore, dispersions can have a noncohesive, salve-like structure. The effect of cross-linking on viscoelastic behavior has been related to the fine structure of the starch (138).

Because cross-linking imparts commercially important viscosity-textural properties, it is employed in conjunction with other types of reactions such as oxidation (87, 89), phosphorylation (91, 114), hydroxyalkylation (91), and esterification (88). The possibility of making highly substituted granular starch derivatives by first cross-linking to produce acetal cross-links, reacting with a monofunctional esterifying or etherifying reagent under aqueous alkaline conditions, and removing the acetal cross-linkages under acid conditions has been claimed (139). The use of combinations of cross-linking bonds that are non-labile (ether linkages) and labile to heat, acid (acetal), or alkali (ester) could provide controlled cooking properties whereby a low viscosity on gelatinization could subsequently be changed to a high viscosity with a short texture. A product of this type would be useful as a thickener in retorted can foods (140). To obtain a particular pattern of viscosity development and high viscosity in a cold-water-dispersible, pregelatinized starch, a dual inhibition treatment is proposed (141). This involves adding 0.03–0.2% sodium trimetaphosphate and sodium chloride to a suspension of granular trimetaphosphate-cross-linked starch at pH 7.8–8.1 prior to drum-drying. Additional cross-linking occurs during the drum-drying.

4. Chemical Properties

Roberts (142) has suggested that starch reacts with epichlorohydrin in a sequence of three reactions catalyzed by alkali to yield a cross-linked network as shown on page 325. A monoglycerol ether of the starch may be produced by

competitive hydrolysis of the starch epoxypropyl ether. Marchessault and co-workers (143) suggest the possibility that another molecule of epichlorohydrin (or more) might react with the starch monoglycerol ether leading to formation of a single cross-link (see page 325).

The amount of epichlorohydrin reacted is estimated by deducting the amount of glycerol formed and residual epichlorohydrin from the total reagent added (144). As little as one cross-link/1000 AGU¹ produced a marked reduction in hot-water solubles. The relationship between the amount of hot-water solubles and reacted epichlorohydrin is nearly linear. Approximately 78% of the epichlorohydrin added reacts with the starch at 25° in 18 h.

Gough and Pybus (145, 146) examined the products of the reaction of epichlorohydrin and alkali-gelatinized wheat starch by acid- and enzyme-catalyzed hydrolysis. Epichlorohydrin both produced cross-links and reacted monofunctionally at the 2-, 3-, 6-positions of the D-glucopyranosyl units. Higher starch-water ratios appeared more favorable to cross-linking.

Marchessault and co-workers (143, 147–150) examined the cross-linking reaction between epichlorohydrin and starch in homogeneous alkaline solutions and heterogeneous granular suspensions. The monoetherification reaction consumes 5–25% of the epichlorohydrin and is strongly dependent on the reaction conditions. Best cross-linking efficiency occurred at high starch concentration and a NaOH/starch mole ratio of 0.5–1.0. High temperature increases the cross-linking rate, but low temperature favors uniformity of product. The extent of the monoether side reaction in the heterogeneous granule reaction is comparable to that in the homogeneous solution reaction. The granule product has a polarization cross, and reaction presumably occurs in the noncrystalline areas. The vapor-phase epichlorohydrin cross-linking reaction is very efficient (147, 148).

Epichlorohydrin-cross-linked granular potato starch has been examined by differential scanning calorimetry and by swelling in solvents (glycerol, water, and dimethyl sulfoxide) (143). Degree of swelling varied regularly with the degree of cross-linking. Calorimetric and x-ray results indicate that the crystallinity of the granule did not change significantly with cross-linking. Water sorption and acid-catalyzed hydrolysis show increased accessibility of the cross-linked granules to small molecules. The percent water in fully hydrated, uncooked, epichlorohydrin-cross-linked corn starch granules, however, is the same as in normal corn starch granules (122). The greater thermal stability of the cross-linked starch as indicated by an increase in the gelatinization temperature measured in the calorimeter is attributed to a decrease in the entropy of melting.

Cross-linking of amylose by epichlorohydrin in a homogeneous reaction in aqueous alkaline solution shows that the reactivity of the C-2 hydroxyl group is much greater than that of the C-6 hydroxyl group, while that of the C-3 hydroxyl group is considerably lower (149). This suggests that the cross-linking reaction proceeds by a reaction similar to etherification of starch by ethylene and propylene oxides. It fosters the assumption that the extent of direct nucleophilic sub-

situation of chlorine is insignificant, favoring the mechanism of the epoxy ring opening reaction.

In contrast to α -amylase digestion of epichlorohydrin-cross-linked, granular potato starch, which decreases as the degree of cross-linking increases, acid-catalyzed hydrolysis increases with increasing cross-linking. It is suggested that cross-linking prevents molecular and structural rearrangement on drying, providing a more open and internally strained structure more accessible to small molecules (150).

A method for determining the adipate content of acetylated starch adipate, produced by the reaction of the mixed linear acetic-adipic anhydride, has been developed (151). The method measures total adipate introduced and does not differentiate the cross-linking adipate di-ester from the mono-ester (page 325). An efficiency of 32.5% is reported for the reaction utilizing 0.1–0.3% adipic acid on the starch. Although methods for the determination of the phosphate content of starch phosphate esters have been available, they have not been suitable for the very low DS of cross-linked distarch phosphates. A method, based on titration of the free acid groups available on the monophosphate and diphosphate ester groups, developed by Mitchell (152) and refined by Koch and co-workers (153), appears useful. Data obtained shows that the cross-linking reaction predominates at a ratio of approximately 3.5:1 when starches are treated with 1% phosphorus oxychloride and 1.5% sodium hydroxide solution for 2 hours at 25° to give a DS of about 0.002. In waxy corn starch, maximum viscosity appears at a DS of approximately 0.0001 phosphate diester. At a DS of 0.005 phosphate di-ester, the products no longer completely disperse on cooking (153).

Potato starch treated with phosphorus oxychloride binds with iodine, but the cross-linked starch forms an iodine complex at a much slower rate than does untreated starch. At high levels of epichlorohydrin treatment of pasted wheat starch, the cross-linked product gives a purple to reddish-brown color indicative of a restricted chain length (145).

5. Uses

Cross-linked starches are used when a stable, high-viscosity starch paste is needed and particularly when the dispersion is to be subjected to high temperature, shear, or low pH. While cross-linking may be the only modification, it is usually employed in combination with other types of derivatization or modification. For resistance to rigorous conditions, high degrees of cross-linking are required. The trend toward continuous cookers generally requires higher cross-linking owing to increased shear and contact with hot surfaces. In extrusion, a higher level of cross-linking is required.

Food starches, especially those made from waxy corn, potato, and tapioca starches, are usually phosphates, acetates, or hydroxypropyl ethers that are cross-

linked to provide appropriate gelatinization, viscosity, and textural properties, including a short, salve-like consistency. Cross-linked starches are also needed for salad dressings to provide the thickening without allowing viscosity breakdown by low pH and the high shear of the homogenization process. Storage stability at the low pH is also increased. In retort sterilization of canned foods, cross-linked starches with a slow gelatinization or swelling rate are used to provide low initial viscosity, high heat transfer, and rapid temperature increase for quick sterilization, with subsequent thickening to provide suspending and texture properties (123, 140, 155–159). Cross-linked starches are used in canned soups, gravies, sauces, baby foods, and cream style corn, as well as in fruit pie fillings, puddings (88, 91, 114, 124, 132, 160–165), and batter mixes for deep-fried foods (166, see also this Volume, Chap. XIX).

Cross-linking of granular starch before drum-drying preserves texture, viscosity, and water-holding power against the shear of the process as well as providing special effects. Drum-dried, cross-linked starches are used to impart a pulpy texture to food systems (167, 168). Drum-dried, cross-linked starches with low amylose content, as in waxy sorghum or corn, are claimed to improve cake volume, crumb softness, and keeping qualities of cakes (169). Acid-converted, cross-linked potato or tapioca starches are drum-dried to produce cold-water-dispersible starches that gel (170).

Cross-linked starches, particularly waxy types or starch derivatives, can be treated with β -amylase to improve low-temperature stability of their aqueous dispersions. Cross-linking is needed to provide optimum thickening and rheological properties in food systems (171, see also this Volume, Chap. XIX).

Cross-linked starches are used in anti-perspirants (172, 173). It has been claimed that cross-linked starch ethers containing carboxymethyl (174) and/or hydroxyalkyl groups (175) are suitable absorbents for personal sanitary applications.

Cross-linked starches are used in alkaline textile printing pastes, contributing high viscosity and the short, non-cohesive texture needed (116). They are used in corrugating adhesives to provide high viscosity under strongly alkaline conditions (116; see also Chapter XX). Other application areas are oil well drilling muds, printing inks, binders for coal and charcoal briquettes, electrolyte-holding media for dry cells (176–178), fiberglass sizing (179–181), and textile sizing (182).

Cross-linking is also used to obtain starches which are not gelatinized on exposure to high temperatures such as sterilization temperatures (183), strongly alkaline solutions, or other conditions where gelatinization would normally occur; such products are generally very high DS granular starch derivatives. Highly cross-linked insoluble granular starches are also used in the preparation of starch xanthates for water treatment (184–186) ion-exchangers (187), stilt material for micro-encapsulated coatings (188), and anti-blocking agents for films (189).

An interesting proposal is the reaction of epichlorohydrin with cross-linked

starch under acid conditions to obtain the 3-chloro-2-hydroxypropyl starch ether that can be further reacted to make an insoluble starch containing anionic, cationic or chelating groups for removal of heavy metal ions from aqueous solutions (190–192).

IV. STARCH ESTERS

1. Introduction

Extensive literature reviews on starch esters have been published (62, 193–202). Starch esters of commercial value are those which provide sol stability and functional properties such as hydrophobic, cationic, or anionic character at relatively low cost. Currently, these esters are the starch acetates and the half-esters of some dibasic carboxylic acids, particularly the alkenylsuccinic acids. As mentioned in the preceding section, the diesters of the dibasic carboxylic acids are valuable because of the cross-linking introduced.

Because the tendency of a starch dispersion to increase in viscosity on cooling and aging and finally to gel is related to the association of the amylose molecules, any treatment which retards or eliminates this crystallization or retrogradation phenomenon will affect stabilization of the starch sol. Acetylation prevents or minimizes association of outer branches of amylopectin molecules. This is of practical value in food applications where it prevents cloudiness and syneresis in aqueous dispersions of waxy starches stored at low temperature. Since a relatively low DS is adequate to achieve this sol-stabilization effect, commercial starch acetates are generally granular and less than 0.2 DS (5% acetyl) (625).

Although there has been considerable interest in the higher DS acetates, particularly amylose acetate, because of their organic solvent solubility, thermoplasticity, and film properties, they have not developed commercially.

2. Preparation of Starch Acetates

A number of reagent-catalyst-solvent systems have been reported, some mainly for laboratory esterification to DS 2–3. Reagents used include acetic acid (203–205), acetic anhydride (88, 95, 200, 201, 206–232), vinyl acetate (233–239), ketene (211, 240, 241), *N*-acetylimidazole (107), ethyl carbonyl-acetic anhydride (242), acetyl guanidine (109), acetyl phosphate (243), and *N*-acetyl-*N'*-methylimidazolium chloride (108).

In many cases, some type of "activation" treatment is used to improve reactivity. All activation treatments involve disruption of the intermolecular hydrogen bonding of granules (193–198, 200, 201, 217). Activation of isolated amylose and amylopectin fractions also involves rupture of intermolecular hydrogen bonds. Reassociation (reorganization) is prevented by insuring that dry-

ing does not take place from a hydrated state; that is, water is removed by azeotropic distillation or by washing with organic solvents such as acetic acid, alcohol, or pyridine.

a. Acetic Acid

Aqueous acetic acid has little effect on starch. Heating starch with 25–100% glacial acetic acid at 100° for 5–13 h introduced 3–6% acetyl groups in the granular product (205). Refluxing dry starch in a large excess of glacial acetic acid dissolves the starch in about 18 h, yielding 44% acetyl content in 296 h (203, 204). Glacial acetic acid may be suitable for producing partially degraded, low-DS starch acetates, but is not efficient for the preparation of DS 2–3 acetates.

b. Acetic Anhydride

Acetic anhydride is generally used for acetylation of starch. It is used alone or with catalysts (203, 210, 215, 216) as well as in conjunction with acetic acid (209, 211–213, 217), pyridine (200, 201, 206–208, 218–221), and dimethyl sulfoxide (223) and in aqueous alkaline solution (88, 95, 207, 231).

Heating starch in acetic anhydride at 90°–140° results in acetylation accompanied by degradation. After 8 h at 140°, 1.8% acetyl is introduced; the acetyl content rises to 8.7% in 15 h and 34% in 74 h (199, 203). Use of acid catalysts, such as sulfuric acid and hydrogen halides, with acetic anhydride produces considerable degradation (194, 199, 202). Alcohol-precipitated, gelatinized potato starch is acetylated to 44.9% acetyl in 1 day in acetic anhydride containing 5% sulfuric acid at 25°, whereas untreated potato starch is 80% unchanged after 6 days (215); corn starch in refluxing acetic anhydride containing sodium acetate yielded a degraded product (43.5% acetyl) in 4 days (216). Ammonium acetate-acetamide catalysis is claimed to yield acetates of DS 2.5–2.8 (244). Potato, corn, and high-amylose corn starches can be fully acetylated with only minor degradation after a 5 h refluxing in fourfold quantities of acetic anhydride and 11% (w/w starch) of sodium hydroxide added as a 50% aqueous solution (226).

Rapid, uniform acetylation of starch by acetic anhydride in liquid sulfur dioxide at 12 bars and 10°–15° is claimed (245). Granular starch acetates having a DS below 0.1 are claimed from heating starch with 8–20% moisture in neat acetic anhydride or with added dimethylformamide (210).

High-amylose corn starch (70%), activated by 1.5% sodium hydroxide added as a 50% solution, can be acetylated to a DS of 0.1–0.31 by treatment with acetic anhydride under acid conditions in a heavy-duty mixer for 30 min at 90–95° (224, 225, 227).

Mixtures of acetic anhydride-acetic acid are slow to acetylate starch at 50° without a catalyst. Acetylation is more rapid in the presence of 1% sulfuric acid,

reaching 40.9% acetyl in 6 h at 50°. Acetylation rate increases with temperature and acid concentration as does degradation (211). Rapid acetylation occurs at reflux without catalyst (211). Almost complete acetylation is claimed for esterification in 1:1 or 3:2 (v/v) acetic anhydride-acetic acid at 95° with 0.2% perchloric acid and 0.6% sulfuric acid (212) or at 105° after dispersing corn starch in 85% phosphoric acid (213). Preparation of granular starch acetates with DS up to 1.5 is claimed by incorporating an inert organic liquid, such as xylene, in the acetic anhydride-acetic acid reaction mixture with a sulfuric acid catalyst (213).

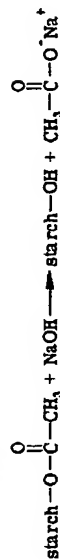
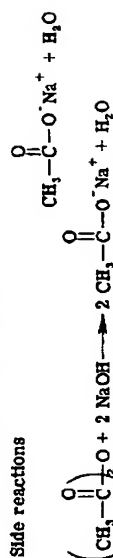
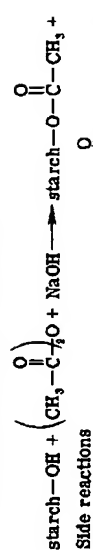
A process was proposed for making amylose and amylopectin triacetates using acetic anhydride-acetic acid at 28°-32° for 6 h (217). Potato amylose is acetylated to a DS of 2.8 with little degradation by reaction in an acetic anhydride-acetic acid mixture at 60°-90° for 3-4 h in presence of 30% poly(styrenesulfonic acid) resin (209).

Acetic anhydride-pyridine is the most common laboratory procedure for acetylation of starch, giving high DS with minimum degradation (194, 207). The system can be used to prepare starch acetates with a wide range of substitution by control of reaction time, temperature, and anhydride concentration (200, 201, 208).

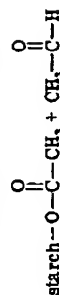
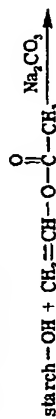
Activation is necessary for reaction in acetic anhydride-pyridine. Refluxing in pyridine at 115° for 1 h activates starch without gelatinization (218). Gelatinization of starch by heating in 60% aqueous pyridine, removing the water as a pyridine azeotrope while adding pyridine, then adding acetic anhydride when the temperature reaches 115° yields a triacetate (200, 201). Another activation method involves disintegration of the starch granules by cooking at 95°-100°, rupture by high shear agitation, and recovery by alcohol precipitation, washing, and drying under reduced pressure (206, 207, 246). The preferred ratio of acetic anhydride:pyridine:starch is 3:2:3.7:1. Activation of starch in formamide has been recommended (219-221, 247). Dispersion in formamide followed by addition of acetic anhydride without the pyridine gives a corn starch diacetate (222). The influence of various activation treatments on high-amylose corn starch (71% apparent amylose) prior to the acetic anhydride-pyridine reaction at 100° to prepare triacetates was examined (226). Dimethyl sulfoxide or hot water cooking were most effective in disrupting the granules.

Low-DS starch acetates can be made by treatment of an aqueous starch suspension with acetic anhydride at pH 7-11 (95, 207, 230-232). Although sodium hydroxide is the preferred alkali, other alkali metal hydroxides, sodium carbonate, trisodium phosphate, and calcium hydroxide are claimed to be suitable (95). Magnesium oxide or hydroxide are claimed as superior alkaline agents for pH control without requiring continuous monitoring (228). At 25°-30°, the pH optimum is 8-8.4, but at 38°, the optimum pH is about 7 (207). Reaction efficiencies of about 70% are obtained.

A. Reaction with acetic anhydride



B. Vinyl acetate



The maximum DS level attainable without gelatinization varies with the particular starch, but the upper limit is about 0.5 DS. To reach a DS of 0.5, it is necessary to repeatedly increase reagent concentrations by filtering the starch from the reaction mixture, resuspending it in 1.25-1.5 parts of water per part of starch, and continuing the acetylation. When higher DS products are required, acetylation of gelatinized starch is preferred (207). A complex between hydroxyl groups and acetic anhydride may precede acetylation (248-250).

It has been suggested that sodium acetate formed as a by-product causes acetyl odors and off-flavors in puddings made from these starch acetates; therefore, the starch acetate must be thoroughly washed to remove by-products and maintain ash content below 0.2% (229).

Acetylation of starch in aqueous suspension by treatment with acetic anhydride in the presence of hydrogen peroxide and ferrous salts is claimed to lower the gelatinization temperature without significant degradation (230). The product may be more readily liquefied by α -amylases.

Acetylation of granular starch in aqueous suspension by acetic anhydride at alkaline pH is used commercially to produce starch acetates of low DS. The type of starch to be acetylated is determined mainly by the properties desired in the product, as well as by the cost of the starch. Potato, wheat, tapioca, corn, and sorghum starches, the last two in regular or waxy varieties, are commonly used. In the United States, regular or waxy corn or sorghum starches are normally chosen for starch acetates. The acetylation treatment may be combined with other modifications such as cross-linking, or a lower viscosity acid-converted or oxidized starch may be used as the base. The starch may come directly from the corn wet-milling process in aqueous suspension or dry starch, such as imported

tapioca or potato starch, may be slurried in water and acetylated. Amylose or amylopectin may be required to provide an acetate with specific properties. The granular starch is the preferred raw material since it can be handled and recovered easily.

c. Ketene

Acetylation of starch with ketene in glacial acetic acid using catalytic amounts of sulfuric acid has been claimed (240). Ketene has also been reacted with starch suspended in acetone or ether with sulfuric acid as the catalyst to introduce 2.2–9.4% of acetyl groups in 0.5–2 h at 25° (240). Gaseous ketene may be used (240). Activation pretreatment of starch is recommended (241). Acetic acid is used for both the pretreatment agent and the reaction medium, although acetone, chloroform, methyl ethyl ketone or tetrachloroethane may also be used as the medium. Acid catalysts are required, the most effective being sulfuric acid; the next most effective is *p*-toluenesulfonic acid. The acid concentration must be regulated to obtain good efficiency without extensive degradation. Reaction at 90° in glacial acetic acid for about 5 h yielded a product containing 42.5% acetyl.

d. Vinyl Acetate

Starch has been acylated by alkaline-catalyzed transesterification with vinyl esters in aqueous medium (233). With vinyl acetate, starch acetate is formed with acetaldehyde as a by-product (234) as shown on page 335.

Acetylation of either granular or gelatinized starch requires the presence of water, since reaction efficiencies of only 2–5% are obtained with less than 10% moisture. Reaction efficiency rises with water content when vinyl acetate is added to starch blended with sodium carbonate and reacted at 24° for one hour. Although the reaction may be run at pH 7.5–12.5 using alkali metal hydroxides, quaternary ammonium hydroxides, ammonium hydroxide and aliphatic amines as catalysts, the preferred range is pH 9–10 where reaction efficiencies of about 65–70% can be expected. Reaction of granular starch suspension in water containing the carbonate buffer gives an acetyl content of 1.4%. Use of the liberated acetaldehyde to cross-link the granular starch at pH 2.5–3.5 is claimed (235). A linear relationship was found between the reaction rate and the amount of sodium hydroxide "adsorbed" by potato starch when it is reacted with vinyl acetate (239).

Vinyl acetate can be used to acetylate amylose in a continuous reactor (237). Amylose suspended in water containing sodium carbonate is mixed with vinyl acetate, and the reaction is done at 166°–177° and 100–140 psi at one gallon per minute throughput. Products have up to 5–8% acetyl content and give solutions with less tendency to gel. Low-DS acetylated potato starch can also be made by a continuous production method (638).

3. Properties of Low-DS Starch Acetates

Microscopic examination of the granules of DS up to 0.2 reveals no discernible difference from native granules. Anionic or cationic dyes will not differentiate starch acetate from the native starch granule (49). A granular starch acetate containing 1.85% acetyl can be completely deacetylated by suspension in water at pH 11 for 4 hours at 25°. The deacetylated starch granule is practically identical to the original. Brabender viscosity curves of corn starch before and after acetylation to 1.8% acetyl are shown in Figure 3. The acetylated starch has a 6° lower gelatinization temperature and a higher hot peak viscosity, reached at a temperature 10° lower than required for the untreated starch. This reduction in gelatinization temperature on acetylation is common to all starches. An aqueous slurry of slightly cross-linked waxy corn starch has a gelatinization temperature of 71°, whereas the same starch with 1.8% acetyl content gelatinizes at 64°, and with 3.5% acetyl, at 62°. Similar effects are reported for corn starch acetate and hydroxyethyl corn starch (49, 55). Acetylated starches are, therefore, more readily dispersed on cooking than are the corresponding native starches.

Corn starch acetates increase in viscosity more slowly than does untreated corn

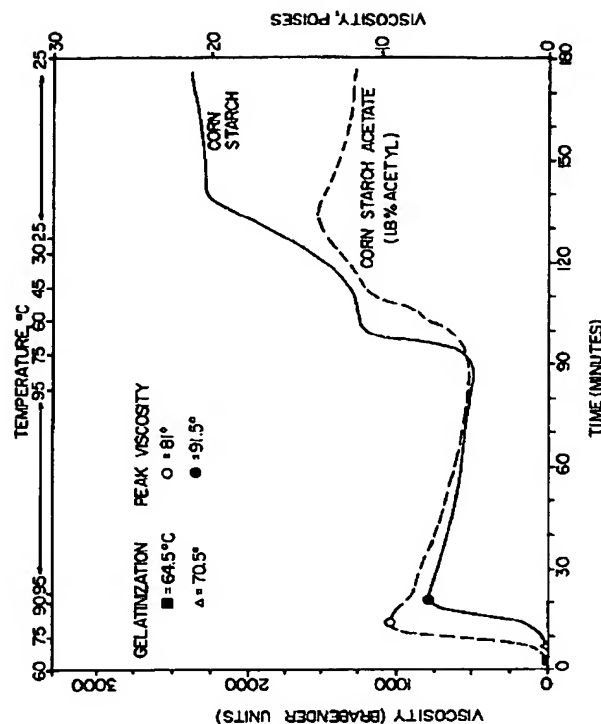


FIG. 3.—Brabender viscosity curves of corn starch and acetylated corn starch (1.8% acetyl). The concentration was 31.5 g of dry starch suspended in 418.5 g distilled water. The pH of the slurry was 5.9. The 350 cm² Brabender cartridge was used.

starch on cooling and do not reach as high a cold viscosity. Potato starch acetates of 0.9–4.23% acetyl content also have lower gelatinization temperatures and hot and cold paste viscosities as the acetyl content increases (251, 252). The ratio of 30° to 80° viscosity decreases with increasing acetyl content up to 2.36% acetyl but does not change significantly at higher acetyl contents.

Use of acetylation to lower gelatinization temperature via interference with molecular association is of value when applied to high-amylose starches. Starches containing at least 50% amylose are so highly associated that they do not gelatinize on cooking in boiling water but require temperatures as high as 160°. The sols produced by high temperature cooking are unstable, tending to gel as the temperature decreases. Acetylation to a DS of 0.1–0.2 lowers the gelatinization temperature so that the product disperses in boiling water and produces relatively stable sols. Substituent groups other than acetates are also effective (223).

Acetylation increases the clarity of sols by increasing the degree of swelling and dispersion of the starch granule as well as reducing retrogradation. Clarity, viscosity and stability of acetylated starches are of value in food, paper, and textile applications (88, 95, 236).

4. Uses of Low-DS Starch Acetates

a. Foods (see also Chapter XIX)

The major use of starch in foods is for thickening. This requires the starch to have a bland taste and impart appealing texture. In food preparation and sterilization, starch may be exposed to a pH as low as 3, high shear in mixing and pumping, high temperatures, temperatures of 5° in the refrigerator or –18° in the freezer and moderately high temperatures in warehousing and transportation. Acetylation alone or in combination with other treatments such as cross-linking can produce starches with the required properties.

Starch acetates containing 0.5–2.5% acetyl groups are used primarily because of their viscosity stability and clarity. This stability is effective under low temperature conditions. Even tapioca, potato, and the waxy corn starches, which have a relatively high degree of stability, require acetylation for low temperature stability. Such stabilization prevents syneresis (weeping or watering) and the development of cloudiness at low temperature (95, 253). Cross-linking is needed to provide desired textural properties and viscosity breakdown resistance.

Cross-linked acetylated starches are used in canned, frozen, baked, and dry foods. They are also used in baby foods and fruit and cream pie fillings in cans and jars to meet the requirement of long shelf life under varying temperature conditions. Frozen fruit pies, pot pies, and gravies maintain their stability under low-temperature storage. In baked goods, the pies, tarts, and filled cakes have greater "weeping" resistance. Acetylated starches are pre-gelatinized for use in

dry mixes and instant gravies and pie fillings. A can-filling starch which has a high viscosity to facilitate uniform can filling and then exhibits viscosity breakdown on heating to increase heat penetration for sterilization and a thin final viscosity is claimed for cross-linked acetylated tapioca, potato, and waxy corn starches (238).

FDA (Food and Drug Administration) regulations permit up to 2.5% acetyl content in starches used in foods. Acetylation in combination with certain other treatments is also permitted (254).

b. Textile, Paper, and Other Uses (see also Chapter XVIII)

Ready dispersibility, viscosity stability and the noncongealing character of pastes make low-DS starch acetates convenient for preparation, storage, handling, and application in textile and paper manufacture.

In textiles, the major market for starch acetates is in warp sizing where they have good yarn adhesion, tensile strength, and flexibility. In addition, the film solubility makes it easily removed (255). Poly(vinyl alcohol) is used in warp sizing because of its high film strength and flexibility, abrasion resistance, and good adhesion. Because of the expense of poly(vinyl alcohol), starch acetates are sometimes blended with it to lower costs and extend properties.

Low-DS starch acetates, with or without cross-linking, are claimed to be effective glass fiber forming sizes (256).

Starch acetates are also used in combination with thermoset resins to produce inexpensive finishes. The starch acetate in the formulation gives weight and "hand" to the fabrics. Starch acetate is used in finishes for inter-liners to give stiffness.

The major use of starch acetates in the paper industry is in surface sizing for improved printability and functional properties by imparting low and uniform porosity, surface strength, abrasion resistance, oil holdout, and solvent resistance, as well as by adhering stray fibers to the substrate (255, 257). Starch acetates compete with oxidized starches, hydroxyethylstarches and low-viscosity starches prepared via enzymes or thermochemical processes. Other competitive products are other film-formers such as carboxymethylcellulose, poly(vinyl alcohol), and alginates (257). When paper containing starch acetates is reintroduced into the paper-making system (by repulping), there is no adverse dispersant effect on the retention of fillers and pigments, as noted with oxidized starches.

In gummed tape formulations, the flexibility, high gloss, and remoisitenability of starch acetate films are useful. A gummed tape containing hypochlorite-oxidized waxy corn starch acetate with 1.5–2% acetyl groups and 0.3–0.5% carboxyl groups is similar to a tape made with animal glue, the industry standard (258).

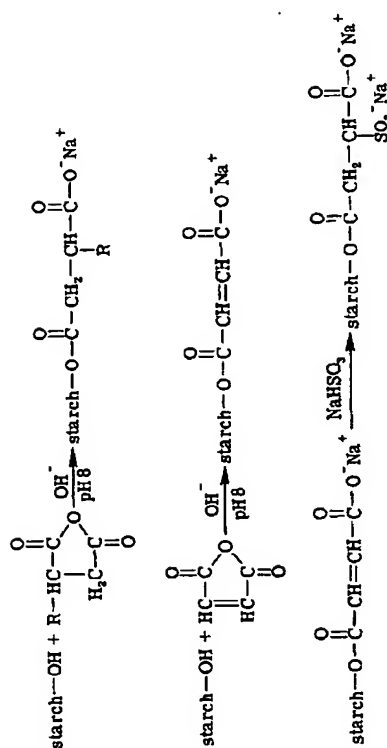
Acetylation has been used to direct amylase hydrolysis to produce maltodex-

6. Acetyl Analysis

The acetyl content of both high- and low-DS starch acetates can be determined by measuring the amount of alkali used in saponification (194, 207, 272). Trans-esterification in anhydrous methanol with sodium methoxide as the catalyst and distillation of the methyl acetate formed is also a suitable analytical method (194, 273). It has the advantage that saponification of the collected methyl acetate is unaffected by traces of nonvolatile acidic materials that may be formed from reducing end-groups in the first method. Combining the latter procedure with gas chromatography of the methyl esters formed can give a qualitative and quantitative analysis for acyl groups in any starch ester. Infrared spectroscopy of the methyl esters can also be used for identification of substituent ester groups. The infrared carbonyl peak at 1724 cm^{-1} has been used to determine the acetyl content in starch acetates (274); the method was also applied to carboxymethyl and cyanoethyl ethers of starch and to starch sulfate. ^1H -nmr can be used to detect and determine acetyl groups as well as other ester groups (275).

7. Miscellaneous Esters

a. Half-Esters of Dicarboxylic Acids



Utilizing the same controlled-pH, aqueous, alkaline starch suspension reaction used to prepare granular starch acetates, low-DS starch half esters of dicarboxylic acids can be prepared (95). Cyclic dibasic acid anhydrides such as succinic anhydride yield starch esters containing a free carboxylate group that increases the water-holding power of the product (95). If a maleate half-ester is made, a sulfonic acid group can be introduced by reaction with bisulfite to give a sulfosuccinate half-ester. This derivative has a lower gelatinization temperature compared to the maleate half-ester and gives clearer, more translucent, stable

trins (259). The higher the DS, the higher is the proportion of oligosaccharides with DP of 30 or greater.

5. Properties of High-DS Starch Acetates

Early work on high-DS starch acetates was done to find a substitute for cellulose acetate (260, 261). However, starch and amylopectin acetates give weak and brittle films, fibers, and molded products (208, 262, 263) and have no economic advantages over cellulose acetates (208, 262–265).

Properties of starch esters with DS of 2–3 depend upon the type of starch, chain length of the substituent, and the conditions of activation and reaction (206, 263, 266). The specific gravity, specific rotation, and melting temperatures generally decrease with increasing acetyl content (261). The specific rotations of the triacetates of whole starch, amylose, and amylopectin from corn are 170 – 174.5° (in chloroform) (206). In pyridine at 22° , the specific rotations of corn, potato, tapioca, wheat, and rice starch triacetates are 151° – 158° (201). The amylose esters of the C_2 to C_{16} alkanolic acids usually have a narrow but higher melting range than do the corresponding amylopectin esters, with whole starch esters intermediate. Triacetates of corn amylose, amylopectin, and whole starch melt at 300° – 301° , 205° – 265° , and 270° – 292° , respectively (263). Melting or softening points of the amylose triesters decrease with increasing length of the alkanolic acid, the melting range of amylose palmitate being 90° – 140° (200, 201, 263, 266).

Solubility characteristics of starch acetates are dependent upon DS and DP (194, 260). Whole starch acetates of up to 15% acetyl content are soluble in water at 50° – 100° and are insoluble in organic solvents (261). Water solubility has been reported for degraded products containing as much as 25% acetyl groups (203, 204). Starch acetates with 40% acetyl content or higher are soluble in aromatic hydrocarbons, halogenated aliphatic hydrocarbons (except carbon tetrachloride), ketones, glycol ethers, and nitroparaffins (261). The aqueous paste disruption activation technique (206) yields more soluble products than either the liquid ammonia or pyridine pretreatment methods (200, 201, 206). Whole starch triacetates do not form true solutions when prepared by the pyridine activation method, but yield dispersions (199, 208). Similar solvent solubilities are reported for corn starch, amylose, and amylopectin triacetates (267).

The thermoplastic molding properties of starch esters, including acetates, have been reported (208). Investigation has been made of amylose triacetate fibers (264, 265), films (262, 263, 266), and plasticization of films (262, 263, 268). X-Ray data on stretched films are available (263, 269). Alkali amyloses with well-defined fiber x-ray diffraction patterns can be prepared by deacetylation of stretched amylose triacetate films (270). Mixed esters of amylose, such as acetate-propionate or acetate-butyrate esters, have been evaluated (271).

dispersions with high water-holding capacity (276). If a cross-linked starch is esterified with a dicarboxylic acid, viscosity stability is obtained. Reaction of cross-linked, thin-boiling, acid-converted or oxidized starch with a polycarboxylic acid anhydride yields an effective warp size (277). A combination corn starch acetate-succinate of DS 0.037 is useful as a corrugating adhesive (278).

Treatment of a starch suspension with a cyclic dicarboxylic acid anhydride containing an hydrophobic substituent group yields products with emulsion stabilizing properties (279). Such an anhydride is 1-octenylsuccinic anhydride. Starches esterified by treatment with up to 3% of this reagent meet the requirements of a "Food Starch-Modified" designation and may be used in food (254). These derivatives are used for emulsion stabilization and encapsulations. If these hydrophobic half-esters are treated in granular form with compounds containing a polyvalent metal ion, such as chromic chloride or aluminum sulfate, a free-flowing water-repellent powder results (280). A product with not more than 2% 1-octenylsuccinic anhydride and a maximum of 2% aluminum sulfate meets the FDA requirements for "Food Starch-Modified" (254). Similar products are recommended as water-repellent encapsulating agents (281). A lipophilic starch derivative suitable for encapsulation of flavoring oils and perfumes and for forming stable emulsions is provided by a waxy corn starch half-ester made with a hydrophobic anhydride and subjected to controlled enzyme hydrolysis with α -amylase to adjust the viscosity before spray-drying (282).

A water-soluble half-ester containing hydrophobic groups, such as starch alkylsuccinate, in combination with gelatin provides a protective overcoat for photographic film (283). This type of product based on an acid-converted starch may be a sizing for paper (284).

Low-molecular-weight, high-DS half-esters made from hydrolyzed starches with DE up to 40 may act as dispersants in aqueous coating formulations such as latex paints (285). Reaction is conducted for 4 h at 82° in an organic medium such as pyridine, formamide, and quinoline, which can act as a solvent for reactants and products. An acylating agent such as octenylsuccinic anhydride is used at ratios of 0.25–3.0 moles per AGU¹. Products of a similar type consisting of mixed esters of mono- and dicarboxylic acids (half-esters) are recommended as dispersants (275, 286).

Products suitable for adhesives are made from thin-boiling, acid-converted or hypochlorite-oxidized starches and dextrans by dry-blending them with dibasic acid anhydrides, such as maleic or succinic anhydride, and heating the mixture at low moisture and 100°–150° to a DS of 0.01–0.1 (287). Mixed hydroxyalkyl ether-esters are made using the hydroxyalkyl dextrin as starting material (288). Dextrin esters of maleic acid copolymers are prepared using ethylene-maleic anhydride or methyl vinyl ether-maleic anhydride copolymers in the dry heat reaction (289).

b. *Starch Ether-Esters*

A water-insoluble, elastic chewing gum base is prepared from hydroxypropylstarch acetate with an MS of 3–6 hydroxypropyl groups and a DS of 1.0–2.5 acetate groups (290). The preparation involves suspending corn or waxy corn starch in toluene, adding a small amount of 25% aqueous sodium hydroxide solution, and then reacting the starch with propylene oxide at 110° for 1–6 h followed by reaction with acetic anhydride at 40°–80° for 1–3 h. After neutralization, the product is purified by extensive washing, steaming, and precipitation from ethanol with water. Hydroxypropyl- or hydroxyethylstarch of MS 0.66 or cellulose of MS 2–8 esterified with acetic or lauric acids to DS 1.2–3 are recommended as gelling agents for organic liquids including jet fuel (291).

Esterification and etherification of high-amylose corn starch can produce granular amphoteric starches with anionic, cationic, and non-ionic groups together with acetyl groups for the preparation of textile warp sizes (292).

c. *Esters for Slow Release*

There is interest in the use of polysaccharides as carriers for the slow release of herbicides and pesticides. Treatment of corn starch with (2,4-dichlorophenoxy)acetyl chloride in pyridine gives a 2,4-D-starch ester. Hydrolysis at pH 6–8 liberates varying amounts of 2,4-D and soluble 2,4-D esters, suggesting its use as a controlled release herbicide (293). However, field tests showed that 2,4-D-starch did not hydrolyze sufficiently to control weed growth. However, various herbicide acid chlorides have been reacted with pregelatinized starch in pyridine to yield esters containing 35–48% active ingredient. One pyridine-based herbicide, picloram, with low volatility and sensitivity to photochemical degradation, was converted to the acid chloride and reacted with starch derivatives and a dextrin. Subsequent work produced pregelatinized starch ester which hydrolyzed more readily than the earlier 2,4-D ester (294). Polysaccharides, including amylose and amylopectin, were dissolved in 5% lithium chloride or bromide solution in dimethylacetamide and treated with the acid chloride or isocyanate pesticide at 90° to obtain polymeric pesticide esters or carbamates (295).

There is interest in polymer-drug adducts in which drugs are linked to macromolecular matrices by covalent bonds which are unstable in the biological environment. Starch trisuccinate converted to a stable benzotriazole appears to offer a good approach (296).

V. HYDROXYALKYLSTARCHES

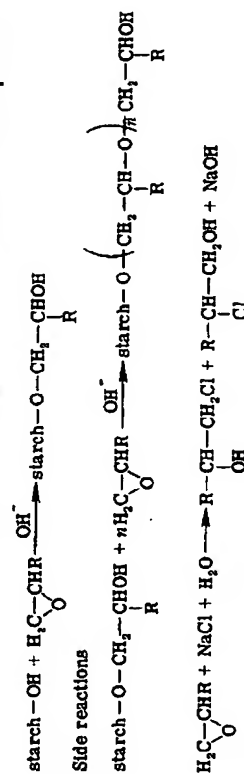
1. Introduction

A limited selection of literature will be included in this section; reference should be made to other reviews (62, 297, 646).

Like the starch acetates, the dispersion stability and nonionic character of the hydroxyalkyl ethers of starch are properties of major commercial interest. Ready availability and low cost also provide commercial interest. Hydroxyethyl- and hydroxypropylstarches are produced in quantities of about 200 million pounds (91×10^6 kg) per year.

2. Preparation

Parents have been issued for the preparation of low-substituted hydroxyalkyl starch ethers (DS 0.05–0.1; 1.3–2.6% hydroxyethyl; 1.8–3.5% hydroxypropyl). (155–158, 161, 298–314). Reaction with alkylene oxide is usually run on a 40–45% starch suspension in water under strongly alkaline conditions at temperatures up to 50°. A blanket of nitrogen is recommended in closed pressure



vessels because of the explosibility of alkylene oxide–air mixtures. Since high alkalinity is needed for good reaction efficiency and since the gelatinization temperature of the granular starch is lowered by the introduction of the hydroxyalkyl groups, salts, such as sodium sulfate or chloride, are added to repress the swelling tendency (313). As the level of hydroxyalkylation increases, more salt is required and, at a DS greater than 0.1, the product becomes difficult to purify because the granules swell as the salt is washed out. To obtain more uniform catalyst distribution, a 30% aqueous sodium hydroxide solution containing 26% salt can be injected into a turbulent flowing starch suspension before charging a tank for the etherification reaction (314).

Hydroxyalkylation can be accomplished by treating starch at 10–13% moisture with gaseous alkylene oxide (307–310). The starch is first impregnated with alkali and a salt such as sodium chloride (308). Another approach employs catalysis by quaternary ammonium bases formed from reaction of tertiary amines with the added epoxide (310). High levels of substitution can be obtained in granular form by these “dry” reactions without concern for swelling (308). Ungelatinized, cold-water-soluble (CWS), hydroxypropylated starches can be prepared using phosphate salts (315) or carboxylic acid salts (316) as catalysts. By using concentrated solutions of strong bases, for example, 50% sodium hydroxide solution, sprayed onto dry starch or by dry-blending starch and an alkali followed by a water spray, the starch is activated sufficiently to react with etherifying agents, including alkylene oxides, to yield ungelatinized CWS starch

ethers (317). Other similar processes with dry starch and cereal flours are reported (318–322).

To prepare a derivative with a DS greater than 0.1–0.3, steps must be taken to reduce swelling. Suspending potato starch in water at 55° and pH about 6.5 raises the gelatinization temperature sufficiently to prevent swelling in a propylene oxide reaction containing sodium sulfate and sodium hydroxide, that will produce 18% hydroxypropyl content (323). It is also claimed that a DS of 0.2–1.5 can be obtained by suspension of the starch in a 5–10% sodium sulfate solution containing 1.5% sodium hydroxide on a starch basis and reacting at 38°, while providing ethylene oxide in small increments over 24-hour periods. Products are ungelatinized and can be washed and filtered (324). Cross-linking of starch is effective in preventing swelling during hydroxyalkylation (182, 325). In one case (182), removal of vinyl sulfone cross-links by cooking in slightly alkaline pH gave a dispersion suitable for warp sizing.

Highly substituted, granular, hydroxyalkyl ethers of starch are readily prepared by suspending the moist, alkaline starch in organic solvents such as lower aliphatic alcohols or ketones (326, 327), higher alcohols (328), and mixtures of organic liquids (329). The alkylene oxide reacts preferentially with the starch, which has adsorbed alkali, rather than with the hydroxyl group of the alcohol. Hydroxyethylation in the range of DS 0.75–1.0 can be obtained without granule swelling. The solubility of the hydroxyalkylstarch in the lower aliphatic alcohols increases with DS. Alcohols can be used to prepare highly substituted products with thermoplasticity and solubility in water for use as adhesives and coatings (330).

Hydroxyalkyl waxy corn starch of MS 0.7–0.9 with water solubility can be made in alcohol solution (326) and used as a cryoprotective agent for human erythrocytes and as a blood plasma volume extender (331, 332).

Cold-water-soluble, hydroxyalkylstarches may be obtained by drum-drying low-DS granular ethers, by gelatinization during or after the hydroxyalkylation reaction and then drum-drying (303, 333, 334), or by reacting to a high DS in solvent to retain the granular form (308). Drum-drying with additives such as borax (sodium tetraborate), boric acid, gum arabic, and sulfate salts are claimed to give improved dispersibility (311, 335–337). Preparation of starch ethers by salting out the product has been recommended (338).

Preparation of di- and poly(hydroxyalkyl) starch ethers via reaction with 2,3-epoxy alcohols is claimed (339). The reaction of styrene oxide with starch to form a phenyl-hydroxyethyl ether is reported (340).

3. Structure of Hydroxyalkylstarches

Considerable work has been reported on the distribution of the substituents in hydroxyethyl- and hydroxypropylstarches (341–350, 639). Merkus and co-workers (341) have reviewed the literature and determined the distribution of

hydroxyethyl groups in hydroxyethylstarches with an MS range of 0.03–1.9. In agreement with other findings, O-2 substitution predominates. In monosubstituted derivatives, 70–80% of the hydroxyethyl groups are reported to be on O-2. Merkus and co-workers (341) suggest that part of the literature differences in substituent location can be attributed to variations in degrees of substitution and/or in the preparation procedures used. O-3 substitution is favored over O-6 substitution by a factor of 2 in products made in water suspension and of MS in the range 0.028–0.041. At high MS (0.84–1.93) and for ethers made in solution reactions, the O-3/O-6 monosubstitution ratio decreases to 0.2. Part of this change can be attributed to more polysubstitution at O-3 as compared to O-6. At levels of substitution of MS about 2, there is a preponderance of O-2 hydroxyethoxyethyl substitution, indicating preference for reaction at the primary hydroxyl group of the O-2 hydroxyethyl group. Calculations of the nominal degree of substitution of derivatized D-glucopyranosyl units shows that the value never reaches 1, not even at high MS levels, for example, the nominal DS is 0.85 at MS 1.93. This indicates that most of the ethylene oxide in the last stage of the reaction goes to polysubstitution on hydroxyethyl substituents already present (341, 351). Even at low MS (0.028–0.041), there is some minimal diethylene oxide substitution (341). This confirms previous observations that there is little formation of poly(ethylene oxide) chains in low-substituted, hydroxyethyl starch ethers (297, 345).

Graft copolymers of poly(alkylene oxides) on starch have been prepared by reaction of the potassium starch alkoxide with ethylene or propylene oxide in dimethyl sulfoxide under anhydrous conditions (354).

Limited data on hydroxypropyl starch is conflicting (348, 349). Leegewater and co-workers (349) reported that over 80% of the hydroxypropyl groups in hydroxypropyl potato starch of DS 0.07 were found at O-2 and 7% at O-6. Similarly, at DS 0.66, the majority of the hydroxypropyl groups were found at O-2. In contrast, for a hydroxypropyl starch, DS 0.47, Gminder and Wagner (348) reported 34% substitution at O-2, 38% at O-3, and 28% at O-6, with 41% of the D-glucopyranosyl units unsubstituted.

The location of the hydroxypropyl groups in a granular hydroxypropyl tapioca starch phosphate of MS 0.045 was deduced from enzyme digestion to be concentrated near the branch points in the amorphous areas of the granule (352).

Infrared and x-ray analysis of hydroxyethyl starches of varying MS showed that substitution of MS 0.18 increases the volume of the unit cell by 4.3% and changes molecular conformation at the equatorial anomeric hydroxyl to axial to relieve ring strain (353).

4. Properties

Low-DS hydroxyethyl- and hydroxypropylstarches behave like low-substituted starch acetates (297). The effects generally increase with increasing DS

X. STARCH DERIVATIVES: PRODUCTION AND USES

(351); thus, the gelatinization temperature decreases (49, 55, 640). The rate of granule swelling and dispersion on cooking increases, clarity (57) and cohesiveness of dispersions increase, and the tendency to increase in viscosity and gel on cooling and aging decreases (640). Hydroxyalkylation also improves low-temperature stability and the clarity, solubility (355), and flexibility of films.

The hydroxyalkyl ether linkage is stable, and substituents remain in place during acid-conversion, oxidation, or dextrinization of the starch derivative. Hydroxyalkyl starches can be used under alkaline conditions as occur in some adhesives or paper coating colors where starch acetates tend to undergo hydrolysis. These non-ionic starch ethers are less affected by electrolytes and pH than are ionic starches (297).

The gelatinization temperature drops as the level of substitution increases. Hydroxyethyl corn starch of MS 0.12 has a birefringence gelatinization temperature range of 45.5°–54.5° compared to corn starch which has a gelatinization temperature range of 62°–70° (49). As MS increases from 0.4 to 1.0, granular hydroxypropylstarch exhibits better dispersibility in cold water. As MS rises above 1.0, solvation by lower aliphatic alcohols increases until the products become soluble in methanol or ethanol (297).

Film prepared from hydroxypropyl high-amylose corn starch (71% apparent amylose; 1.11% hydroxypropyl, intrinsic viscosity 1.02) is water-soluble, transparent, and impermeable to oxygen at 25° over a wide range of humidities (356). Hydroxypropylation reduces tensile strength of the film but increases elongation and burst strength and maintains folding endurance. Plasticization with 5% glycerol is not beneficial.

With hydroxypropyl potato starch of MS 0.02–0.45, pancreatic digestibility decreased exponentially with increasing MS (357, 358). Pancreatic α -amylase digestibility is decreased to a greater extent by hydroxypropyl groups in wheat starch than by acetyl groups (359). Digestibility of gelatinized wheat starch ethers decreased to 55% at MS 0.17 while digestibility of the corresponding granular starch ethers increased from 31% to 61% (360). The difference in digestibility may be explained by retrogradation in the gelatinized sample. On partial digestion, there is a concentration of the hydroxypropyl groups in the low-DP oligosaccharide fraction. The relative amount of this fraction increases with increasing MS (360). Pancreatic α -amylase hydrolysis of hydroxyethylstarch, MS 0.55–0.94, showed decreased hydrolysis rates with increasing MS with indication that substitution at O-2 conferred more resistance to the enzyme-catalyzed hydrolysis than did O-6 substitution (347).

5. Uses

Hydroxyethylstarches of low MS have been widely used in the paper industry, particularly for surface sizing and coating (65, 255, 257, 361, 362, see also this

Volume, Chap. XVIII). In surface sizing, they provide strength and stiffness to the paper as well ink hold-out.

Low-MS hydroxyethylstarches are used as a binder, alone or in combination with synthetic polymers, in pigmented paper coatings (363-366). They provide good leveling and viscosity stability in the coating color. The high water-holding properties control binder penetration into the base sheet (366). These starches provide high binder strength for the pigment and adhesion to the base stock. Printing quality of the resulting coating is good. Hydroxyethylated starches are claimed to be superior for the preparation of wet-rub-resistant coatings using glyoxal (367, 368). They are suitable for admixture with synthetic polymers in clay coating (369). Molecular weight distributions of acid-converted hydroxyethylstarches used in coating have been determined (370, 371).

The low gelatinization temperature of hydroxyethylstarch is of value when granular starch is added to the wet end of the paper-making machine and expected to gelatinize when the paper sheet passes over the drying rolls. The starch granules swell and spread through the sheet and increase internal strength (361).

The water-holding and filming properties of hydroxyethylated starches are useful in adhesives such as bag pastes and case-sealing, label, and envelop adhesives (297). Some is used for the carrier portion of corrugating adhesives (372).

Low-substituted hydroxyethylstarches are used in warp sizing, alone or in blends with poly(vinyl alcohol). The stable viscosity and filming properties give the hydroxyalkylstarches use in liquid laundry starches or, when pregelatinized, as instant laundry starches (297). They may be used in aerosol spray starch formulations (373).

Hydroxypropylstarches are of importance in food applications where they provide viscosity stability in the food thickener and insure water-holding under low-temperature storage conditions. These starches are usually cross-linked to obtain desired texture and resistance to the high temperatures, low pHs, and shear degradation often encountered in processing. They may be used in granular form or as pregelatinized, cold-water-soluble products. They may be used in conjunction with other thickeners, for example, with carrageenan in milk systems to be retorted (374) and with xanthan gum in salad dressing (375). They are used as thickeners in gravies, sauces, fruit pie fillings, and puddings where they must impart a smooth, thick, clear, non-granular texture that will hold up under various storage temperatures, including freezing, and also impart no taste (376). Hydroxypropyl tapioca starch is a good starch for frozen pudding (377). Hydrolysis of hydroxypropylstarches gives low viscosity, bland-tasting, low bulk-density maltodextrin-like materials (378, 379). Hydroxypropylated high-amylose starch produces an edible, water-soluble film coating for foods (380). Hydroxypropylstarches with specific levels and types of treatment have been designated as "Food Starch - Modified" under the F.D.A. regulations for use in foods (254, this Volume, Chap. XIX).

There has been considerable interest in the use of hydroxyethylstarch as a blood volume extender and as a cryoprotective agent for erythrocytes (331, 351, 381).

6. Analysis

To determine total hydroxyalkyl content, use is normally made of the standard Zeisel hydriodic acid digestion as modified by Morgan (382) and Lortz (383, 384). A number of attempts have been made to couple the Zeisel digestion with gas chromatography (385, 386). One procedure for cellulose ethers which uses xylene and adipic acid to catalyze the hydriodic acid cleavage of the ether substituent to form an alkyl iodide appears quite effective for starch ethers (386). Another method uses pyrolysis-gas chromatography (387). Concentrated sulfuric acid digestion of hydroxypropylstarch releases propionaldehyde, which is determined spectrophotometrically (388). ¹H-nmr may also be used to determine hydroxypropyl DS (389). O-Hydroxyalkyl-D-glucose obtained by hydrolysis with concentrated sulfuric acid can be determined by gas chromatography (341, 342, 347, 349, 390).

VI. STARCH PHOSPHATE MONOESTERS

1. Preparation

a. Orthophosphates

Sodium phosphate monoesters can be prepared by heating intimate blends of 10% moisture starch and orthophosphates (particularly a mixture of mono-hydrogen and dihydrogen phosphates) at pH 5-6.5 for 0.5 to 6 h at 120°-160° (391-400).



In a typical laboratory reaction, starch is suspended in water containing dissolved phosphate salts, and the mixture is stirred for 10-30 min and filtered. The filter cake is air-dried or dried at 40°-45° to 5-10% moisture and then heat-reacted. Representative data is shown in Table I. Using these reaction conditions, products up to 0.2 DS can be made (391, 397).

It is not commercially feasible to dry the starch-phosphate salt filter cake at low temperature. Kerr (124) suggests that typical continuous-belt driers of the Proctor and Schwartz type are satisfactory. In this equipment, starch can be dried at a temperature of 48°-124° without gelatinization. The temperature of the starch-phosphate salt mixture should not exceed 60°-70° until the moisture content has been reduced to about 20%. This prevents gelatinization and minimizes undesirable side reactions such as hydrolysis of the phosphate reagents (124).

Table I

Phosphorylation with Orthophosphates				
	$\text{NaH}_2\text{PO}_4/\text{Na}_2\text{HPO}_4^a$ g	Starch/water, g/mL	Temp./time, °C/h.	%P/DS ^b Ref.
A	23.2/—	162/240	160°/0.5	0.45/— 394
B	34.5/96	180/190	150°/4.0	1.63/— 393
C	57.7/83.7	100/106	155°/3.0	2.50/0.15 397
D	7.5/11.2	50/65	145°/2.5	0.56/0.03 398

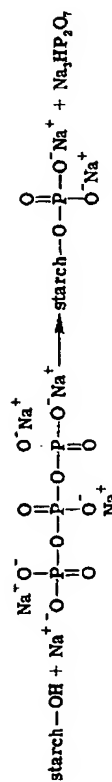
^a A, B, C used $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$; B used $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$; C, $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$. A, B, C: Filter cakes were air-dried. C: filter-cake dried overnight at 40–45° in a forced-draft air oven; then at 65° for 90 min. B, D: heat-reacted in vacuum oven. A, C: heated with continuous stirring (for example, in a stainless steel beaker placed in an oil bath). Slurry pH: A(5.5), B(—), C(6.1), D(6.5).

^b %P = bound phosphorus; DS = degree of substitution.

Treating starch with a proteinase such as pepsin or papain appears to enhance sodium phosphate retention by the starch granule (401). Products containing 6–12% phosphorus can be prepared by slurring starch in 45–55% orthophosphate solutions at 50°–60° followed by filtration, drying, and heat reaction at 140°–155° (400). Similarly, starch has been phosphorylated with tetrasodium pyrophosphate (TSPP) (124) or mixtures of TSPP with orthophosphates (402) or phosphoric acid (403, 404). Alkyl pyrophosphates such as dimethyl or bis(2-ethylhexyl) pyrophosphate can be used to phosphorylate starch in dry reactions (406). Monostarch phosphates can be prepared by heating mixtures of starch and ammonium metaphosphate or ammonium polyphosphate at 110°–140° for 1 to 4 h at a pH range of 5–9 (405). The use of sodium (or other alkali metals) metaphosphate (124) or polyphosphate (405) in the same pH range results in substantial cross-linking. For these alkali metal salts, the reaction pH should be less than 5 for mono ester formation (124); pHs lower than 4 promote hydrolysis of the starch (407).

b. Sodium Triphosphate

Starch can be phosphorylated with sodium triphosphate (STP) (124, 391, 397, 408, 409).



The initial pH of the STP–starch mixture is typically 8.5, decreasing to 7 or less after heat reaction. For example, a starch filter cake containing 5% STP is

dried at 60° to about 12% moisture, then heated at 120°–130° for 1 h. A water-washed sample contains 0.37% phosphorus. Extending the heat treatment to 2 hours yields a product with 0.47% phosphorus (124). The amount of STP retained in the starch filter cake is adjusted by varying the amount of STP and/or the amount of water in the slurry.

In an alternative procedure, acidified (pH 4.2–4.8) 20–36% aqueous solutions of STP were used to impregnate starch filter cakes (408, 409). The starch-STP blends were dried in a flash drier to 5–8% moisture followed by heat reaction at 110°–130° or the filter cake-STP blends were dried directly at 130° to 6% moisture or less. Products containing 0.07–0.10% phosphorus were produced.

The distribution of the phosphate ester groups in a STP-derivatized starch (heat-reacted at 150°, 0.30% bound phosphorus) was determined (410).

Position	% Distribution of phosphate groups
O-2	28
O-3	9
O-6	63

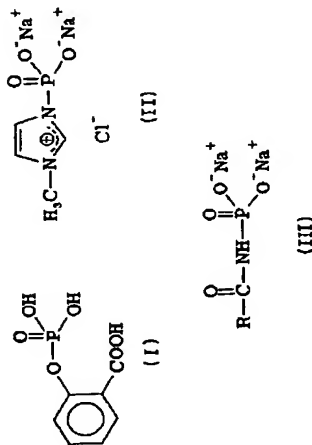
c. Urea-Phosphates

Combinations of urea and phosphate salts have been used to modify starch (411–422). Urea appears to act as a catalyst promoting higher reaction efficiencies and more rapid reaction between the starch and phosphates (412, 414). The final product viscosities are higher when urea is present (411–417). Using 2–5% urea (on starch), varying amounts of orthophosphates, pH 4–8, and heating times of several hours at 140°–160° gave 1 to 5% bound phosphorus (411). Hjertstad (412) indicated that urea (or other amides) plus orthophosphate and starch produced nitrogen-substituted phosphate groups, but Alexander (414) found that 2–3% urea and 1–6% sodium triphosphate produced derivatives containing phosphate (<0.3% bound phosphorus) and carbamate groups (1.3–1.7% nitrogen).

In other work, the ratio of nitrogen to phosphorus was controlled by heating the reaction mixture under reduced pressures. When the vacuum was decreased, nitrogen substitution, cold-water solubility, and the rate of attainment of maximum dispersion viscosity increased (413).

d. Organic Phosphorylating Reagents

Starch phosphate monoesters can be produced by aqueous reactions with *o*-carboxyaryl phosphates (I, 423), *N'*-substituted, *N*-phosphorylimidazole salts (II, 424), or *N*-acylphosphoramidic acid salts (III, 425). Typically, reactions are run at 30°–50°. I and III react at pH 3–8 while II requires more alkaline reaction conditions, (pH 11–12).



Starch phosphonate ether derivatives have been claimed by alkali-catalyzed slurry reactions with vinyl phosphonates, vicinal halohydroxyalkane phosphonates, or vicinal epoxyalkane phosphonates (426).

Derivatizing reagents have also been prepared by reacting 2-alkyl-2-oxazolines with phosphorus oxychloride (phosphoryl chloride) (427). Reactions with starch at pH 11.4 and at 40° for 16 hours produce derivatives containing anionic, phosphoramidic acid groups. Corn starch products yield dispersions that are clear and stable.

Starch monophosphate esters with degrees of substitution of 1.75 are obtained by heating starch at 120° with a mixture of trialkylamine and tetrapolyphosphoric acid in *N,N*-dimethylformamide. The starch is recovered by alcohol precipitation (428).

2. Properties

Dispersions of corn starch monophosphates have clarity, high viscosity, a long cohesive texture, and stability to retrogradation (391). Viscosity is controlled by manipulating the amount of phosphate salts, reaction temperature, time, and pH (391, 393). Starch phosphate derivatives are useful as emulsification agents (124, 405, 406), and dispersions of the phosphate esters have freeze-thaw stability (391).

3. Uses

a. Paper (see also Chapter XVIII)

Starch phosphates find use in the paper industry as wet-end additives providing improved strength and filler retention (361, 391, 401, 407, 429). Alum must be present in the system for optimum performance (391, 407). Starch phosphates have outstanding dispersing properties for clay-satin white coating colors (430). Low viscosity urea-phosphate starches are useful in paper coating, particularly

when they are combined with satin white pigment (391, 431, 432). For example, tapioca phosphate of 34 cP at 25° and 15% concentration is prepared by heating a mixture of 1000 parts of tapioca starch, 75 parts of orthophosphoric acid, and 140 parts of urea at 126° for 45 min. Coating colors consisting of the urea-phosphate starches, satin white, and china clay SPS yield excellent wet-rub resistance of 90–91 in the Adams test. If satin white is eliminated, the wet-rub resistance decreases to zero (431). Combinations of phosphoric acid and urea are approved for starch modification for internal sizing, surface sizing, and coating under the FDA indirect food additive regulations (433).

Amphoteric starches prepared by phosphorylating cationic derivatives are useful wet-end additives (408, 409, 423–426, 434, 435). Starch phosphates have also been used in emulsions with ketene dimers as internal sizing agents for paper (436, 437).

b. Textile

Compositions containing 50–90 parts of starch monophosphate and 10–50 parts of poly(vinyl alcohol) or polyacrylate are useful textile sizing agents of cotton, polyester-rayon, and polyester-cotton yarns (438). Phosphorylated starches are useful thickeners for textile printing, providing improved uniformity and penetration for printing cotton (439).

c. Adhesives (see also Chapter XX)

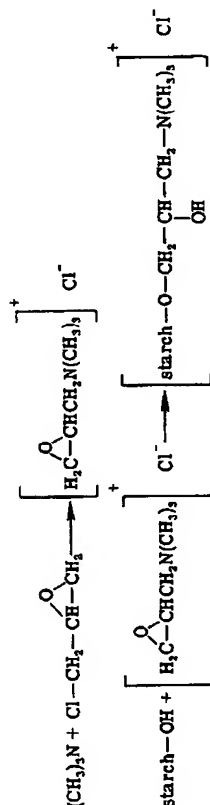
Adhesives with improved storage stability for use in corrugated paperboard are prepared by blending starch monophosphate with native starch, borax, sodium hydroxide, and water (440). In another adhesive, Neoprene rubber latexes are combined with 0.01–10% starch phosphate to produce adhesives with good, rapid bond strength. In one example, a latex containing about 4.2% starch phosphate is used to bond wood pieces. Shear strengths of 108, 290, and 464 lb/in.² (7.59, 20.4, and 32.6 10⁴ kg/m²) were observed after 10 minutes, 24 h, and 10 days, respectively. Without the starch, shear strengths were 9, 249, and 440 lb/in.² (0.633, 17.5, and 30.9 10⁴ kg/m²) for the same time periods (441).

d. Scale Inhibition

Starch phosphates prevent or inhibit scale-forming deposits when added to water in amounts of 10 mg/L (442, 443). In a similar application, 10–50 ppm of starch phosphate was added to salt brine containing 2–5.5 g of calcium sulfate. The starch phosphate prevented precipitation of the calcium sulfate and enabled recovery of high purity salt (444, 445).

e. Flocculation

A flocculant for coal washery tailings has been prepared by drum-drying a starch slurry containing sodium dihydrogenphosphate and heat-treating the re-



A wide variety of tertiary amines can be used, but the ones most reactive with epichlorohydrin contain at least two methyl groups. Care must be taken to remove or substantially reduce, by vacuum distillation or solvent extraction, any residual epichlorohydrin or by-products such as 1,3-dichloropropanol that can cross-link the starch and reduce dispersibility and effectiveness of the cationic starch. The use of tertiary amine salts of weak acids, such as acetic acid, in aqueous reactions with epichlorohydrin is claimed to result in lower by-product formation (472).

The chlorohydrin form of the reagents is stable in water and can be rapidly converted to the "active" epoxide form by the addition of sodium hydroxide.



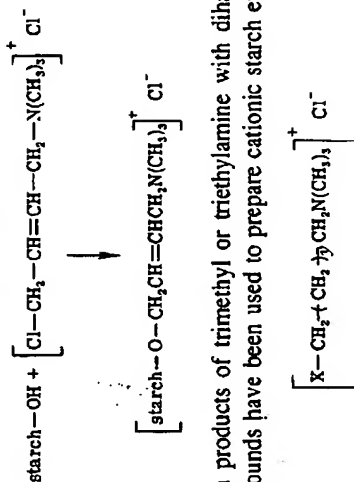
Recently, an investigation was made on the aqueous reaction of 3-chloro-2-(hydroxypropyl)trimethylammonium chloride with corn starch (473). Products ranging from 0.01 to 0.07 DS were made in the presence of sodium hydroxide and sodium sulfate to prevent swelling of starch. Using a sodium hydroxide to reagent mole ratio of 2.8:1, a reagent to starch mole ratio of 0.05:1, and a 35% starch concentration at 50°, the reaction efficiency was 84% after 4 h. Lower temperatures required longer reaction times. The concentration of both reagents and starch influence the reaction efficiency. A DS of 0.02–0.04 is satisfactory for most paper uses.

These non-volatile quaternary ammonium reagents are particularly useful for dry or "semi-dry" reactions with starch. The epoxide or glycidyl forms of the reagents can react with starch without alkaline catalyst, but at 120°–150° for 1 h (474, 475). Reaction efficiencies of 75–100% are obtained if an alkaline catalyst is used in combination with the quaternary ammonium reagents (476, 477). Alkaline-catalyzed reactions can be run at lower temperatures, typically 70°–80° for 1–2 h.

The reagents can also be prepared by quaternizing a tertiary amine with allyl chloride and reacting the resulting *N*-allyl quaternary ammonium chloride with hypochlorous acid to produce the cationizing reagent (478–480). Preparation of 3-chloro-2-(hydroxypropyl)triethylammonium chloride was claimed by the reac-

tion of triethylamine with α -chloroglycerol followed by treatment with hydrogen chloride dissolved in acetic anhydride (481). Quaternary pyridinium salt–starch derivatives have also been described (482).

A similar class of cationizing derivatives is represented by the 4-halo-2-butenyltrialkylammonium halides (483–486).



The reaction products of trimethyl or triethylamine with dihalo substituted alkylene compounds have been used to prepare cationic starch ethers (487).



X = Cl, Br; y = 1–3

c. Aminoethylated Starches

Although commercially useful cationic starches are primarily the tertiary amino and quaternary ammonium derivatives, other types have received some attention. Ethylenimine reacts with starch to yield the 2-aminoethyl ether (488).



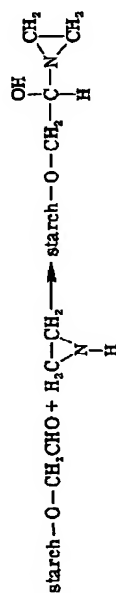
Typical processes involve mixing the dry, or semi-dry, starch with gaseous ethylenimine at 75°–120° without catalysts (489–491). Poly(ethylenimine) is a by-product in these reactions, but its formation can be reduced or eliminated by control of the temperature and pressure of the reaction. Aminoalkylation of starch in inert solvents such as carbon tetrachloride and benzene has been accomplished with the use of an aziridine–sulfur dioxide complex (492).

Cationic starches have been prepared by treating aqueous starch suspensions with ethylenimine in the presence of ethylene oxide and an alkaline catalyst at 35° for 16 hours (493). Without ethylene oxide, almost no cationic groups are introduced. Organic halides or esters of strong acids may be used in place of an alkylene oxide.

The efficiency of the reaction of ethylenimine with starch is increased if a tertiary amino starch (494) derivative is used. In this case, ethylenimine side chains are grafted onto the substituent tertiary amino alkyl groups or onto starch hydroxyl groups.

Aziridiny starch derivatives can be prepared by reacting starch containing keto or aldehyde substituents with ethyleneimine in water at temperatures below 20° (495).

Similar derivatives of acid-modified corn starch can be prepared by sodium hydroxide-catalyzed reactions with *N*-(4-chloro-2-butenyl)aziridine or *N*-(1-hydroxy-2,3-epoxypropyl)aziridine. The resulting derivatives can be reacted further and are useful as latent cross-linking agents (495).



The preparation of aminoalkylated starches has also been claimed by reduction of cyanoalkylated starch with sodium borohydride, hydrazine hydrate, sodium hydrosulfite, and 1,3-dihydroxypropanone in aqueous ammonium hydroxide (496).

d. Cyanamide-Starch

Reaction of starch with a disubstituted cyanamide in the presence of a strong base yields a starch iminodialkyl carbamate (497). Protonation of the imino

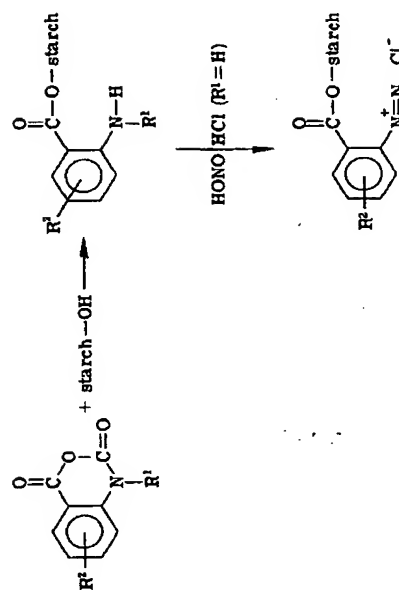


nitrogen atom forms the ionic salt which makes the substituent stable to hydrolysis. Similar derivatives have been prepared using cyanamide salts ($\text{R} = \text{H}$) (498–502). Iminoalkyl derivatives produced in granular form by normal slurry reactions tend to be cross-linked. Cyanamide-starch pastes tend to thicken with time. Phosphate salts and aluminum sulfate appear to stabilize the pastes (501).

The dry, starch-cyanamide reaction products become water-insoluble with storage, but can be redispersed in boiling water at $\text{pH} < 2$ (503). Storage-stable cyanamide-starch has been produced by neutralizing the reaction mixture to $\text{pH} 1.0$, followed by gelatinization and drum-drying to 10% moisture (504). Similar products are prepared by drying the granular derivatives at 40°–50° after neutralization to $\text{pH} 3.0$ (505, 506).

e. Starch Anthranilates

Cationic starch esters have been prepared by reacting starch with isatoic anhydride and its derivatives (507–511). The starch slurry reaction is conducted at pH of 7.5–9.0. The product (when $\text{R}_1 = \text{H}$) can be diazotized by treatment with nitrous acid (507, 508) and subsequently coupled with aromatic type compounds to produce azo dyes (507) or further reacted with starch to form cross-linked derivatives (508).



f. Cationic Dialdehyde Starch

Dialdehyde starch has served as a base for preparing cationic derivatives. The aldehyde groups are reacted with hydrazines or hydrazides (512–514). The reaction with betaine hydrazide hydrochloride is illustrated (515).

Dialdehyde starch at 15% concentration in water is reacted with 3–5% reagent. The initial pH of 4.5 decreases to 2.5–3.2 after reaction. The dispersion forms an initial gel which liquefies with continued heating at 90°–95°. To obtain a dispersion which remains fluid at 25°, holding times of at least 2.3–3.0 hours at 95° are required. Cationic dialdehyde starch has also been prepared by reacting unmodified starch with *N,N*-dimethylaminoethyl chloride or with the quaternary ammonium reagents described previously, followed by oxidation with periodic acid to form the dialdehyde starch (515).



g. "In Situ" Cationization

Generally, commercial cationic starches are prepared by slurry reactions with a cationizing reagent followed by recovery of the starch in granular form.

Another method involves the simultaneous cooking and reaction of the starch at $\text{pH} 8$ with a monofunctional reagent such as β -diethylaminoethyl chloride or 3-chloro-2-(hydroxypropyl)trimethylammonium chloride or another of the reagents previously described (516, 517). Typically, temperatures of 100°–160° are used.

Many derivatizing agents require the preparation of epichlorohydrin-ammonia (518, 519) and/or amine condensates (520–523). Similar polymeric, polyamine reagents have been prepared by the reaction of alkylene dihalides and amines

3. Properties

The gelatinization temperature of cationic starches decreases as the number of cationic substituent groups increases (460). The dispersions show improved stability and clarity (463). Zeta potential measurements of typical cationic starches show a net positive charge at pH 4–9 (458).

4. Uses

a. Paper: Wet-End Additive (see also Chapter XVIII)

Electrochemical affinity of cationic starch for negatively charged cellulose fibers results in nearly 100% irreversible adsorption of the starch derivative (561). The cationic starch acts as an ionic bridge between the cellulose fibers and mineral fillers and pigments. The preferential adsorption of cationic starch on pulp fines results in increased retention of fines and an improvement in strength by inclusion of fines with long fibers in a cohesive network (458). This can lead to a better drainage as well (562).

A typical paper-making furnish contains numerous additives used to affect sheet properties or control the runnability of the furnish on the paper machine (562). The most popular additive, alum (563), may be present in various amounts (564) and can adversely affect the pulp adsorption of cationic starch (561, 565, 566). To improve performance under varying conditions, numerous cationic starches were developed (361). Amphoteric starches (434, 435, 545, 546) are examples of products developed to yield consistent performance under varying paper mill conditions. Use of a starch quaternary ammonium ether (0.033 DS) and an anionic poly(acrylamide) (2% dry basis on starch) starch derivative improves pigment retention with alum at pH 4–5 (567).

In another process, filler retention and strength are increased by coating Kain particles with 5% of a starch quaternary ammonium ether and incorporating the product into a pulp system at a 30% concentration (568).

In addition to new products and experimentation with combinations of additives (563, 569–571) and changes in papermaking systems, better wet-end control methods have been devised to ensure optimum performance from cationic starches (564).

b. Sizing

Of increasing importance in paper making is the use of cationic starch to emulsify synthetic sizing agents such as alkyl ketene dimers or alkenyl succinic anhydrides (458, 572–578).

In addition to their wet end use, cationic starches are used as surface sizing agents. The irreversible, ionic attraction to cellulose fibers results in lower penetration as well as lower BOD in mill effluents (257, 579, 580). Cationization is often combined with degradative reactions such as oxidation, acid-catalyzed

hydrolysis, or dextrinization because starch dispersions with high solids are required. An improved surface sizing starch is made by combining the film-forming properties of high-amylose starch with cationic modification (581).

c. Coating

As a coating binder, cationic starch offers increased strength due to the electrochemical binding of clay to fiber (582, 583). However, if the amine content is too high, agglomeration or even coagulation of the clay can occur. A starch product containing amine (0.015–0.025 DS) and carboxyl substituents (0.5–1.5% COOH groups) yields good binding and shock-free clay dispersion (548–551).

d. Textile

Both cationic and amphoteric starches find use as warp sizing agents (552–557, 584). The starch size provides lubrication and abrasion resistance. Cationic quaternary ammonium starches in combination with a cationic lubricant and an emulsified wax have been used to provide protective coatings for glass fibers during twisting and texturizing (585).

e. Flocculation

Cationic starches are effective agents for flocculating aqueous suspensions of negative organic or inorganic particles such as clay, titanium dioxide, coal, carbon, iron ore, silt, anionic starch, and cellulose (564, 586, 587). In an effort to develop improved products, high-DS types are prepared by reacting gelatinized starch with quaternary amine reagents (588, 589). Derivatives of 50–90 fluidity are used because they will form higher solids dispersions. Products with 0.4 to 0.5 DS (588) and >0.7 DS (589) have been prepared. They can be used directly or purified by dialysis, ultrafiltration, or ion exchange (589). These products, as well as lower DS (0.15–0.25 amine substituent DS) derivatives of hypochlorite-oxidized starch (590, 591) or acid-converted waxy maize starch (592), are effective in treating raw primary sludge.

f. Miscellaneous

Starch quaternary ammonium ethers of 0.1–0.45 DS are useful demulsifiers for breaking water-in-oil and oil-in-water emulsions (593). Both tertiary amino and quaternary ammonium starches act as reducing and suspension agents for preparing antihalation layers for photographic film from manganese dioxide (594). Insoluble (cross-linked) cationic starches are effective in removing heavy metal anions such as chromate, dichromate, ferrocyanide, ferricyanide, molybdate, and permanganate from industrial effluents (595). A tertiary aminoalkyl derivative of high-amylose corn starch is useful as the active ingredient in a hair-holding spray (596).

5. FDA Regulations

The Federal Food and Drug Administration has regulations (433) for modified starches that may be in any material that comes in contact with food. Cationic starches may be present as additives in the paper or paperboard food package. The cationizing reagents that may be used in the preparation of these starches are (4-chlorobutene-2)-trimethylammonium chloride, β -diethylaminoethyl chloride, or 2,3-(epoxypropyl)trimethylammonium chloride. The regulation specifies maximum treatment levels, and, in some cases, the use of the derivative and the addition levels in a particular application.

6. Analysis

Cationic starches are conveniently analyzed by determining the nitrogen content using the Kjeldahl method (597, 598).

When starch is analyzed, a dextrose blank is commonly used. Unmodified starches typically contain very small amounts of protein corresponding to nitrogen values of less than 0.1% (455). An examination of 17 commercial cationic starches indicated a nitrogen content ranging from 0.18% to 0.37% (361).

VIII. OTHER STARCH DERIVATIVES

1. Introduction

Some starch derivatives are commercially manufactured and sold on a small scale; others appear to have properties of commercial interest. Two derivatives in these categories are mentioned here.

2. Starch Xanthates

The reaction of polysaccharides with carbon disulfide under strongly alkaline conditions to form xanthates has long been known. Interest in starch xanthates



has been rekindled by work showing their effectiveness in removal of heavy metal ions from process waters (184-186, 599-602) and as reinforcing agents in rubber (603-608) and slow-release encapsulating agents for pesticides (609-612).

Early work on starch xanthation reported the distribution of xanthate groups (613) and the effect of various alkali metal hydroxides (614) on the distribution. A continuous process for xanthation of starch involving the metered addition of granular starch, sodium hydroxide solution and carbon disulfide to a continuous,

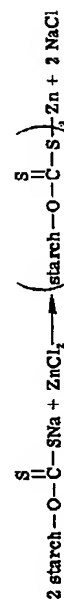
high-shear mixer-reactor and discharging the viscous paste after roughly 2 minutes reaction time has been developed (185, 615, 616). Low-concentration pastes (10%) with DS 0.05-0.15 xanthate were prepared in a low-powered mixer using only small amounts of alkali (185, 617-620). For the water treatment, the product is prepared in granular form by using starch cross-linked sufficiently with epichlorohydrin to resist gelatinization in the strongly alkaline xanthation reaction.

The distribution of the xanthate groups on the starch xanthates (DS 0.12 or 0.33) prepared by the rapid continuous process has been shown to take place initially at O-2 and O-6 (621). Xanthation at O-3 is much slower. The product of 0.12 DS showed the presence of unsubstituted AGU¹ and their mono- and di-xanthates in mole ratios of 34:4:0.1, while the corresponding ratios for the DS 0.33 product were 32:13:1. The monosubstituted component of the DS 0.33 product showed a 67:27:6 ratio for O-6:O-2:O-3 xanthate substitution while the corresponding ratio for the DS 0.12 product was 56:44:0 (621). Thus, the primary hydroxyl group on C-6 is most readily xanthated under the conditions of the continuous reaction (613, 621).

Aqueous solutions of the starch xanthates are unstable owing to both hydrolysis and oxidation. Dry xanthates usually have sufficient moisture to be unstable. Starch xanthate powder, stable for several months at 25° or indefinitely at 0°, has been made by decreasing the alkali content before spray-drying (622). The magnesium salt of starch xanthate has room temperature stability for several months if the xanthate is completely in the magnesium salt form. Storage at 0° increases stability. A moisture content below 2% is important for storage stability (184, 185, 602). This instability and the difficulty in handling, storage and transportation has been a major commercial drawback to an otherwise useful product.



Starch xanthates can be oxidized to cross-linked xanthides, which are stable and effective in heavy metal ion removal from water (619, 620, 623). Metal ions, such as zinc, copper, and iron react with starch xanthate to form insoluble metal dithiocarbonates; the preferred ion is zinc (617, 619, 620).



Addition of the soluble starch xanthate (DS 0.05-0.75) to the wet end of the paper-making process with precipitation on the pulp through xanthide or metal starch dithiocarbonate formation results in increases in the dry and wet tensile, burst, and fold strength with a reduction in tear strength (619, 620, 624). Simi-

larly, mixing starch xanthates with elastomer latexes, coprecipitating the two polymers by cross-linking the starch via oxidation or with zinc ions, and destabilizing the latex gives a curd which dries to a friable starch xanthide-encased rubber crumb. Milling gives coalescence of the rubber to form a continuous phase with starch xanthide reinforcement. The products are light in color (603-607, 625).

The starch xanthates are most effective in removing heavy metal ions from waste waters (184, 599-602).

3. Dialdehyde Starch

Large scale use of dialdehyde starch has not developed because of high cost. A comprehensive coverage has been given in various reviews (63, 626-628, 647). Periodic acid and periodates oxidize 2,3-glycol structures specifically to aldehydes and this reaction has been used for structure determination of carbohydrates (629-632). The degree of oxidation is determined by the amount of periodate used and, hence, can be controlled (628). Even though the periodate-oxidized starch is called "dialdehyde starch" (DAS), very few free aldehyde groups are present; rather the principal structures are hydrated hemialdal and intra- and intermolecular hemiacetals (626, 628, 631). However, DAS reacts as an aldehyde-containing material; the latent aldehyde groups react with bisulfite ions, alcohols, amines, hydrazines, hydrazides, and other reagents that condense with aldehydes. Sodium bisulfite dialdehyde starch yields tetrahydroxybenzoquinone via glyoxal on alkaline degradation (642). Chlorous acid oxidizes the aldehyde groups to carboxylic acids, yielding a polycarboxylate polymer (87, 626).

For small scale production of DAS in a range of oxidation levels, a chemical process has been proposed in which the spent oxidant is oxidized with alkaline hypochlorite to sodium paraperiodate. This salt can be recovered by filtration for recycling (635). A commercial process renews the periodate ion by electrolytic oxidation (627, 628, 633, 634).

The proposed uses of DAS are based on its activity as a reactive polymeric polyaldehyde that acts as a cross-linking agent for substrates containing hydroxyl, amino, and imino groups. Thus, it is useful in imparting temporary and permanent wet strength to paper (636), in hardening gelatin, in tanning leather, and in making water-resistant adhesives (626, 627). Reactions to prepare cationic DAS have been reported (637).

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CHAPTER XI

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I. INTRODUCTION

Rapidly increasing prices and dwindling supplies of petroleum have intensified interest in natural products as alternative sources of energy and raw materials for the chemical industry. Starch, a polysaccharide produced in great abundance in nature, is a prime candidate for use as a raw material because it is available at a low cost and can be converted readily into a variety of useful monomeric and polymeric products by chemical and biochemical means.

While there is social and economic controversy over using such natural products as starch for chemicals instead of food, the fact remains that the United States produces more carbohydrate than is needed for a balanced diet. The six major cereal grain crops produced in 1977 contained 400 billion pounds of starch. Most of this starch was fed to animals, despite tests showing better weight gain with higher protein feeds (1). Hence, the nutritional value of grain products is enhanced by removing part of the starch or by fermenting the starch to alcohol, leaving a high quality feed known as distillers dried grains. However, these processes are economically feasible only when a market exists for the starch or starch-derived products. Hundreds of products from and applications of starch

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